

INTERNATIONAL COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C. 20231  
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing: 08 September 2000 (08.09.00)	
International application No.: PCT/GB00/00703	Applicant's or agent's file reference: SMC 60341/WO
International filing date: 28 February 2000 (28.02.00)	Priority date: 01 March 1999 (01.03.99)
Applicant: ELLIS, Gordon, Lee et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International preliminary Examining Authority on:  
17 July 2000 (17.07.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was  
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer:  J. Zahra Telephone No.: (41-22) 338.83.38
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## PCT

## REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference  
(if desired) (12 characters maximum) SMC 60341/WO**Box No. I TITLE OF INVENTION**

Pigment Printing Composition

**Box No. II APPLICANT**

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

Avecia Limited  
Hexagon House  
Blackley  
Manchester M9 8ZS  
United Kingdom

☐ This person is also inventor.

Telephone No.

0161 740 1460

Facsimile No.

0161 721 5801

Teleprinter No.

State (that is, country) of nationality:  
GBState (that is, country) of residence:  
GBThis person is applicant  
for the purposes of:☐ all designated  
States☒ all designated States except  
the United States of America☐ the United States  
of America only☐ the States indicated in  
the Supplemental Box**Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)**

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

ELLIS, Gordon Lee  
PO Box 42, Hexagon House  
Blackley  
Manchester M9 8ZS  
United Kingdom

This person is:

☐ applicant only☒ applicant and inventor☐ inventor only (If this check-box  
is marked, do not fill in below.)State (that is, country) of nationality:  
GBState (that is, country) of residence:  
GBThis person is applicant  
for the purposes of:☐ all designated  
States☐ all designated States except  
the United States of America☒ the United States  
of America only☐ the States indicated in  
the Supplemental Box☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.**Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE**The person identified below is hereby/has been appointed to act on behalf  
of the applicant(s) before the competent International Authorities as:☒ agent☐ common representativeName and address: (Family name followed by given name; for a legal entity, full official designation.  
The address must include postal code and name of country.)

SCHMITT Maja  
Intellectual Property Group  
Avecia Limited  
PO Box 42, Hexagon House  
Blackley, Manchester M9 8ZS  
United Kingdom

Telephone No.

0161 721 1154

Facsimile No.

0161 721 5801

Teleprinter No.

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.



## Continuation of Box No. III FURTHER APPLICANTS AND/OR (FURTHER) INVENTORS

*If none of the following sub-boxes is used, this sheet should not be included in the request.*

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

YEATES, Stephen George  
PO Box 42, Hexagon House  
Blackley  
Manchester M9 8ZS  
United Kingdom

This person is:

- ☐ applicant only  
☒ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:  
GB

State (that is, country) of residence:  
GB

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

ANNABLE, Tom  
PO Box 42, Hexagon House  
Blackley  
Manchester M9 8ZS  
United Kingdom

This person is:

- ☐ applicant only  
☒ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:  
GB

State (that is, country) of residence:  
GB

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

MAHON, Paul Francis  
PO Box 42, Hexagon House  
Blackley  
Manchester M9 8ZS  
United Kingdom

This person is:

- ☐ applicant only  
☒ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:  
GB

State (that is, country) of residence:  
GB

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

RICHARDS, Stuart Nicholas  
21 Fieldway  
Frodsham  
Cheshire  
WA6 6RO  
United Kingdom

This person is:

- ☐ applicant only  
☒ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:  
GB

State (that is, country) of residence:  
GB

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.



**Box No.V DESIGNATION OF STATES**

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

**Regional Patent**

- ☒ **AP ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ **EA Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ **OA OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

**National Patent (if other kind of protection or treatment desired, specify on dotted line):**

- |   |  |   |
|---|--|---|
| <input checked="" type="checkbox"/> <b>AE</b> United Arab Emirates                  | <input checked="" type="checkbox"/> <b>LR</b> Liberia  |   |
| <input checked="" type="checkbox"/> <b>AL</b> Albania                               | <input checked="" type="checkbox"/> <b>LS</b> Lesotho  |   |
| <input checked="" type="checkbox"/> <b>AM</b> Armenia                               | <input checked="" type="checkbox"/> <b>LT</b> Lithuania  |   |
| <input checked="" type="checkbox"/> <b>AT</b> Austria                               | <input checked="" type="checkbox"/> <b>LU</b> Luxembourg   |   |
| <input checked="" type="checkbox"/> <b>AU</b> Australia                             | <input checked="" type="checkbox"/> <b>LV</b> Latvia   |   |
| <input checked="" type="checkbox"/> <b>AZ</b> Azerbaijan                            | <input checked="" type="checkbox"/> <b>MD</b> Republic of Moldova  |   |
| <input checked="" type="checkbox"/> <b>BA</b> Bosnia and Herzegovina                | <input checked="" type="checkbox"/> <b>MG</b> Madagascar   |   |
| <input checked="" type="checkbox"/> <b>BB</b> Barbados                              | <input checked="" type="checkbox"/> <b>MK</b> The former Yugoslav Republic of Macedonia                      |   |
| <input checked="" type="checkbox"/> <b>BG</b> Bulgaria                              |  |   |
| <input checked="" type="checkbox"/> <b>BR</b> Brazil                                | <input checked="" type="checkbox"/> <b>MN</b> Mongolia   |   |
| <input checked="" type="checkbox"/> <b>BY</b> Belarus                               | <input checked="" type="checkbox"/> <b>MW</b> Malawi   |   |
| <input checked="" type="checkbox"/> <b>CA</b> Canada                                | <input checked="" type="checkbox"/> <b>MX</b> Mexico   |   |
| <input checked="" type="checkbox"/> <b>CH and LI</b> Switzerland and Liechtenstein  | <input checked="" type="checkbox"/> <b>NO</b> Norway   |   |
| <input checked="" type="checkbox"/> <b>CN</b> China                                 | <input checked="" type="checkbox"/> <b>NZ</b> New Zealand  |   |
| <input checked="" type="checkbox"/> <b>CU</b> Cuba                                  | <input checked="" type="checkbox"/> <b>PL</b> Poland   |   |
| <input checked="" type="checkbox"/> <b>CZ</b> Czech Republic                        | <input checked="" type="checkbox"/> <b>PT</b> Portugal   |   |
| <input checked="" type="checkbox"/> <b>DE</b> Germany                               | <input checked="" type="checkbox"/> <b>RO</b> Romania  |   |
| <input checked="" type="checkbox"/> <b>DK</b> Denmark                               | <input checked="" type="checkbox"/> <b>RU</b> Russian Federation   |   |
| <input checked="" type="checkbox"/> <b>EE</b> Estonia                               | <input checked="" type="checkbox"/> <b>SD</b> Sudan  |   |
| <input checked="" type="checkbox"/> <b>ES</b> Spain                                 | <input checked="" type="checkbox"/> <b>SE</b> Sweden   |   |
| <input checked="" type="checkbox"/> <b>FI</b> Finland                               | <input checked="" type="checkbox"/> <b>SG</b> Singapore  |   |
| <input checked="" type="checkbox"/> <b>GB</b> United Kingdom                        | <input checked="" type="checkbox"/> <b>SI</b> Slovenia   |   |
| <input checked="" type="checkbox"/> <b>GD</b> Grenada                               | <input checked="" type="checkbox"/> <b>SK</b> Slovakia   |   |
| <input checked="" type="checkbox"/> <b>GE</b> Georgia                               | <input checked="" type="checkbox"/> <b>SL</b> Sierra Leone   |   |
| <input checked="" type="checkbox"/> <b>GH</b> Ghana                                 | <input checked="" type="checkbox"/> <b>TJ</b> Tajikistan   |   |
| <input checked="" type="checkbox"/> <b>GM</b> Gambia                                | <input checked="" type="checkbox"/> <b>TM</b> Turkmenistan   |   |
| <input checked="" type="checkbox"/> <b>HR</b> Croatia                               | <input checked="" type="checkbox"/> <b>TR</b> Turkey   |   |
| <input checked="" type="checkbox"/> <b>HU</b> Hungary                               | <input checked="" type="checkbox"/> <b>TT</b> Trinidad and Tobago  |   |
| <input checked="" type="checkbox"/> <b>ID</b> Indonesia                             | <input checked="" type="checkbox"/> <b>UA</b> Ukraine  |   |
| <input checked="" type="checkbox"/> <b>IL</b> Israel                                | <input checked="" type="checkbox"/> <b>UG</b> Uganda   |   |
| <input checked="" type="checkbox"/> <b>IN</b> India                                 | <input checked="" type="checkbox"/> <b>US</b> United States of America                                       |   |
| <input checked="" type="checkbox"/> <b>IS</b> Iceland                               |  |   |
| <input checked="" type="checkbox"/> <b>JP</b> Japan                                 | <input checked="" type="checkbox"/> <b>UZ</b> Uzbekistan   |   |
| <input checked="" type="checkbox"/> <b>KE</b> Kenya                                 | <input checked="" type="checkbox"/> <b>VN</b> Viet Nam   |   |
| <input checked="" type="checkbox"/> <b>KG</b> Kyrgyzstan                            | <input checked="" type="checkbox"/> <b>YU</b> Yugoslavia   |   |
| <input checked="" type="checkbox"/> <b>KP</b> Democratic People's Republic of Korea | <input checked="" type="checkbox"/> <b>ZA</b> South Africa   |   |
|   | <input checked="" type="checkbox"/> <b>ZW</b> Zimbabwe   |   |
| <input checked="" type="checkbox"/> <b>KR</b> Republic of Korea                     | Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet: |   |
| <input checked="" type="checkbox"/> <b>KZ</b> Kazakhstan                            | <input checked="" type="checkbox"/> <b>CR</b> Costa Rica   | <input checked="" type="checkbox"/> <b>DM</b> Dominica                    |
| <input checked="" type="checkbox"/> <b>LC</b> Saint Lucia                           | <input checked="" type="checkbox"/> <b>MA</b> Morocco  | <input checked="" type="checkbox"/> <b>TZ</b> United Republic of Tanzania |
| <input checked="" type="checkbox"/> <b>LK</b> Sri Lanka                             |  |   |

**Precautionary Designation Statement:** In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)





**Supplemental Box** *If the Supplemental Box is not used, this sheet should not be included in the request.*

1. If, in any of the Boxes, the space is insufficient to furnish all the information: in such case, write "Continuation of Box No. ..." [indicate the number of the Box] and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:

- (i) if more than two persons are involved as applicants and/or inventors and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;
- (ii) if, in Box No. II or in any of the sub-boxes of Box No. III, the indication "the States indicated in the Supplemental Box" is checked: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;
- (iii) if, in Box No. II or in any of the sub-boxes of Box No. III, the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;
- (iv) if, in addition to the agent(s) indicated in Box No. IV, there are further agents: in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV;
- (v) if, in Box No. V, the name of any State (or OAPI) is accompanied by the indication "patent of addition," or "certificate of addition," or if, in Box No. V, the name of the United States of America is accompanied by an indication "continuation" or "continuation-in-part": in such case, write "Continuation of Box No. V" and the name of each State involved (or OAPI), and after the name of each such State (or OAPI), the number of the parent title or parent application and the date of grant of the parent title or filing of the parent application;
- (vi) if, in Box No. VI, there are more than three earlier applications whose priority is claimed: in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI;
- (vii) if, in Box No. VI, the earlier application is an ARIPO application: in such case, write "Continuation of Box No. VI", specify the number of the item corresponding to that earlier application and indicate at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed.

2. If, with regard to the precautionary designation statement contained in Box No. V, the applicant wishes to exclude any State(s) from the scope of that statement: in such case, write "Designation(s) excluded from precautionary designation statement" and indicate the name or two-letter code of each State so excluded.

3. If the applicant claims, in respect of any designated Office, the benefits of provisions of the national law concerning non-prejudicial disclosures or exceptions to lack of novelty: in such case, write "Statement concerning non-prejudicial disclosures or exceptions to lack of novelty" and furnish that statement below.

Continuation of Box IV


FAWKES, David Melville  
MAYALL, John  
NELSON, Michael Andrew  
PUGSLEY, Roger Graham  
REVELL, Christopher  
SHELLER, Alan

All of Intellectual Property Group, Avecia Limited, PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS, United Kingdom

LOCKE, Timothy John

of Intellectual Property Group, Avecia Limited, PO Box 2, Belasis Avenue, Billingham, Cleveland TS23 1YN, United Kingdom



<b>Box No. VI PRIORITY CLAIM</b>		<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: regional Office	international application: receiving Office
item (1) 1 March 1999 (01/03/99)	9904599.9	GB		
item (2) 29 October 1999 (29/10/99)	9925515.0	GB		
item (3) 11 November 1999 (11/11/99)	9926645.4	GB		
<input checked="" type="checkbox"/> The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): 3				
<i>* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.</i>				
<b>Box No. VII INTERNATIONAL SEARCHING AUTHORITY</b>				
<b>Choice of International Searching Authority (ISA)</b> (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):		<b>Request to use results of earlier search; reference to that search</b> (if an earlier search has been carried out by or requested from the International Searching Authority):		
ISA / EPO		Date (day/month/year)	Number	Country (or regional Office)
<b>Box No. VIII CHECK LIST; LANGUAGE OF FILING</b>				
This international application contains the following number of sheets: request : 05 description (excluding sequence listing part) : 30 claims : 02 abstract : 01 drawings : 00 sequence listing part of description : 00 <b>Total number of sheets : 38</b>		This international application is accompanied by the item(s) marked below: 1. <input checked="" type="checkbox"/> fee calculation sheet 2. <input type="checkbox"/> separate signed power of attorney 3. <input type="checkbox"/> copy of general power of attorney; reference number, if any: 4. <input type="checkbox"/> statement explaining lack of signature 5. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s): 6. <input type="checkbox"/> translation of international application into (language): 7. <input type="checkbox"/> separate indications concerning deposited microorganism or other biological material 8. <input type="checkbox"/> nucleotide and/or amino acid sequence listing in computer readable form 9. <input type="checkbox"/> other (specify):		
Figure of the drawings which should accompany the abstract:		Language of filing of the international application: ENGLISH		
<b>Box No. IX SIGNATURE OF APPLICANT OR AGENT</b>				
Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request). For Avecia Limited ELLIS Gordon Lee, YEATES Stephen George, ANNABLE Tom, MAHON Paul Francis, RICHARD Stuart Nicholas   SCHMITT Maja				

For receiving Office use only	
1. Date of actual receipt of the purported international application:  3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:  4. Date of timely receipt of the required corrections under PCT Article 11(2):  5. International Searching Authority (if two or more are competent): ISA /	2. Drawings: <input type="checkbox"/> received:  <input type="checkbox"/> not received:  6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.

For International Bureau use only
Date of receipt of the record copy by the International Bureau:





**PCT**

11 APR 2001

**INTERNATIONAL PRELIMINARY EXAMINATION REPORT**

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference SMC 60341/WO		<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/GB00/00703	International filing date (day/month/year) 28/02/2000	Priority date (day/month/year) 01/03/1999
International Patent Classification (IPC) or national classification and IPC C09D11/00		
Applicant AVECIA LIMITED et al.		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"><li>I <input checked="" type="checkbox"/> Basis of the report</li><li>II <input type="checkbox"/> Priority</li><li>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</li><li>IV <input type="checkbox"/> Lack of unity of invention</li><li>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</li><li>VI <input type="checkbox"/> Certain documents cited</li><li>VII <input type="checkbox"/> Certain defects in the international application</li><li>VIII <input type="checkbox"/> Certain observations on the international application</li></ul>		
Date of submission of the demand  17/07/2000		Date of completion of this report  06.04.2001
Name and mailing address of the international preliminary examining authority:   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized officer  Sperry, P  Telephone No. +49 89 2399 8298 



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/00703

## I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, pages:**

1-30 as originally filed

**Claims, No.:**

1-20 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):





# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/00703

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

## **V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

### **1. Statement**

Novelty (N)	Yes:	Claims	1-20
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-20
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-20
	No:	Claims	

### **2. Citations and explanations see separate sheet**



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/GB00/00703

**R Item V**

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

Claims 1 to 20 meet the requirements of Art. 33(2)-(4) PCT since the claimed subject-matter is not disclosed or suggested by the prior art cited in the International Search Report.




# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>SMC 60341/WO</b>	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. <b>PCT/GB00/00703</b>	International filing date (day/month/year) <b>28/02/2000</b>	Priority date (day/month/year) <b>01/03/1999</b>
International Patent Classification (IPC) or national classification and IPC <b>C09D11/00</b>		
Applicant <b>AVECIA LIMITED et al.</b>		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of    sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> <li>I    <input checked="" type="checkbox"/> Basis of the report</li> <li>II   <input type="checkbox"/> Priority</li> <li>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</li> <li>IV   <input type="checkbox"/> Lack of unity of invention</li> <li>V    <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</li> <li>VI   <input type="checkbox"/> Certain documents cited</li> <li>VII <input type="checkbox"/> Certain defects in the international application</li> <li>VIII <input type="checkbox"/> Certain observations on the international application</li> </ul>		
Date of submission of the demand  <b>17/07/2000</b>	Date of completion of this report  <b>06.04.2001</b>	
Name and mailing address of the international preliminary examining authority:   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  <b>Sperry, P</b>  Telephone No. +49 89 2399 8298	





**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB00/00703

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, pages:**

1-30 as originally filed

**Claims, No.:**

1-20 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):





**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB00/00703

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes: Claims 1-20
	No: Claims
Inventive step (IS)	Yes: Claims 1-20
	No: Claims
Industrial applicability (IA)	Yes: Claims 1-20
	No: Claims

**2. Citations and explanations**  
**see separate sheet**



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/GB00/00703

**Re Item V**

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

Claims 1 to 20 meet the requirements of Art. 33(2)-(4) PCT since the claimed subject-matter is not disclosed or suggested by the prior art cited in the International Search Report.



# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>SMC 60341/WO</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/GB 00/ 00703</b>	International filing date (day/month/year) <b>28/02/2000</b>	(Earliest) Priority Date (day/month/year) <b>01/03/1999</b>
Applicant <b>AVECIA LIMITED et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 02 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

### 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.



# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/GB 00/00703

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 822 238 A (DU PONT) 4 February 1998 (1998-02-04) page 3, line 30-57 page 4, line 6-29 page 4, line 30 -page 5, line 19 page 5, line 35-40 ---	1,10-13, 17-20
A	US 4 925 885 A (ROSTHAUSER JAMES W ET AL) 15 May 1990 (1990-05-15) column 11, line 38-41; claims 1-3 ---	1,10
A	EP 0 796 901 A (TOYO INK MFG CO) 24 September 1997 (1997-09-24) cited in the application -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- \*"A" document defining the general state of the art which is not considered to be of particular relevance
- \*"E" earlier document but published on or after the international filing date
- \*"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*"O" document referring to an oral disclosure, use, exhibition or other means
- \*"P" document published prior to the international filing date but later than the priority date claimed

- \*"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

4 May 2000

15/05/2000

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Miller, A





# INTERNATIONAL SEARCH REPORT

on patent family members

International Application No

PCT/GB 00/00703

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0822238	A	04-02-1998	JP 10095857 A	14-04-1998
US 4925885	A	15-05-1990	CA 1338294 A	30-04-1996
			EP 0324370 A	19-07-1989
			JP 2003465 A	09-01-1990
EP 0796901	A	24-09-1997	JP 9249838 A	22-09-1997
			US 5814685 A	29-09-1998



**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C09D 11/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/52106</b> <b>(43) International Publication Date:</b> 8 September 2000 (08.09.00)
<b>(21) International Application Number:</b> PCT/GB00/00703 <b>(22) International Filing Date:</b> 28 February 2000 (28.02.00)  <b>(30) Priority Data:</b> 9904599.9 1 March 1999 (01.03.99) GB 9925515.0 29 October 1999 (29.10.99) GB 9926645.4 11 November 1999 (11.11.99) GB  <b>(71) Applicant (for all designated States except US):</b> AVECIA LIMITED [GB/GB]; Hexagon House, Blackley, Manchester M9 8ZS (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ELLIS, Gordon, Lee [GB/GB]; Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB). YEATES, Stephen, George [GB/GB]; Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB). ANNABLE, Tom [GB/GB]; Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB). MAHON, Paul, Francis [GB/GB]; Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB). RICHARDS, Stuart, Nicholas [GB/GB]; Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB).		<b>(74) Agents:</b> SCHMITT, Maja; Avecia Limited, Intellectual Property Group, Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB) et al.  <b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PIGMENT PRINTING COMPOSITIONS  <b>(57) Abstract</b>  A composition comprising the components: (a) a hydrophilic polymer having a number average molecular weight less than 30,000; (b) a hydrophobic polymer having a number average molecular weight more than 40,000; (c) pigment; and (d) liquid medium, and use of the composition in ink-jet printing.		



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## PIGMENT PRINTING COMPOSITIONS

The invention relates to compositions containing pigments and to their use in inks for ink-jet printing.

Ink-jet printing involves printing an image onto a substrate using ink droplets ejected through a fine nozzle onto a substrate without bringing the fine nozzle into contact with the substrate.

There are many demanding performance requirements for colorants and inks used in ink-jet printing. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust which would block the tip of the fine nozzle. The inks should also be stable to storage over time without decomposing or forming a precipitate which could also block the fine nozzle.

Thermal and piezoelectric ink-jet printers are widely used, thus there is a need for inks, suitable for use in both types of printers, having high colour strength and giving images having a high light-fastness and water-fastness when printed on a typical substrate, especially plain paper.

It is known to include aqueous resins emulsions in ink formulations to improve water-fastness of resultant prints. For example EP 0882 771 discloses an aqueous ink-jet recording liquid containing a pigment and a solubilised resin emulsion, and EP 796 901 discloses an aqueous pigment ink jet-recording liquid containing an aqueous dispersion resin consisting of a core/shell acrylic polymer.

It has now been found that combinations of a pigment with a low molecular weight hydrophilic polymer and a high molecular weight hydrophobic polymer in a liquid medium results in a composition which is suitable as an ink for use in thermal and piezo ink-jet printers, shows stability over a range of conditions and the resultant prints show improved water-fastness, light-fastness, optical density and smear resistance over the use of a single resin component.

Thus, according to the present invention there is provided a composition comprising the components:

- (a) a hydrophilic polymer having a number average molecular weight less than 30,000;
- (b) a hydrophobic polymer having a number average molecular weight more than 40,000;
- (c) pigment; and
- (d) liquid medium.

The number average molecular weight ( $M_n$ ) for components (a) and (b) may be measured by any of the well known techniques, preferably by gel permeation chromatography ("gpc"). The gpc method used for determining  $M_n$  preferably comprises applying the polymer to a chromatography column packed with cross-linked



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polystyrene/divinyl benzene, eluting the column with tetrahydrofuran at a temperature of 40°C and assessing the Mn of the polymer compared to a number of a polystyrene standards of a known Mn. Suitable cross-linked polystyrene/divinyl benzene chromatography columns are commercially available from Polymer Laboratories.

5 As an alternative to the gpc method for determining Mn one may use other methods, for example multi-angle light scattering.

Preferably the Mn of component (a) is less than 20,000, more preferably less than 12,500 and especially less than 10,000. Preferably the Mn of component (a) is more than 500. Preferably the Mn of component (b) is more than 60,000 more preferably more than 70,000. Preferably the Mn of component (b) is less than 10 million, more preferably less than 2 million.

The hydrophilic and hydrophobic polymers may each independently be homopolymers or copolymers. Preferably the hydrophilic and hydrophobic polymers are copolymers.

15 Component (a) is preferably hydrophilic by virtue of the presence of ionic and/or non-ionic water dispersing groups in the hydrophilic polymer. The hydrophilic polymer is preferably prepared by polymerising one or more monomers having water-dispersing groups, optionally with one or more monomers which are free from water-dispersing groups. The nature and level of water-dispersing groups in the polymer influences  
20 whether a solution, dispersion, emulsion or suspension is formed on dissipation of the hydrophilic polymer in aqueous media. Preferably the level of monomers having water-dispersing groups is from 5 to 80% by weight of the hydrophilic polymer. Preferably the level of monomers having water-dispersing groups is at least 5% by weight greater in the hydrophilic polymer than the level of monomers having water-dispersing groups in the hydrophobic polymer. For example, if the level of monomers having water-dispersing groups is 5% by weight of the hydrophobic polymer then the level of monomers having water-dispersing groups in the hydrophilic polymer is preferably at least 10% by weight of the hydrophilic polymer. More preferably the level of monomers having water-dispersing groups is at least 10% by weight greater in the hydrophilic polymer than the level of monomers having water-dispersing groups in the hydrophobic polymer. Preferably a solution is formed on dissipation of the hydrophilic polymer in water, although a minor amount of the hydrophilic polymer may be insoluble in water and exist as dissipated particles when mixed with aqueous media or water.

Water-dispersing groups are preferably pendant to the main polymer backbone.  
35 Preferred ionic water-dispersing groups are anionic water-dispersing groups, especially carboxylic, phosphonic and or sulphonic acid groups. Preferred non-ionic water-dispersing groups are polyoxyalkylene groups, more preferably polyoxyethylene groups.

A small segment of the polyoxyethylene group can be replaced by a oxypropylene segment and/or oxybutylene segment, however the polyoxyethylene group should still  
40 contain oxyethylene as a major component. When the water-dispersing groups in the



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hydrophilic polymer are predominantly polyoxyethylene groups, the polyoxyethylene group content preferably does not exceed 25% by weight, more preferably does not exceed 15% by weight, based on the total weight of the hydrophilic polymer.

The anionic water-dispersing groups are preferably fully or partially in the form of a salt. Conversion to the salt form is optionally effected by neutralisation of the polymer with a base, preferably during the preparation of the hydrophilic polymer and/or during the preparation of the composition of the present invention. If anionic water-dispersing groups are used in combination with a non-ionic water-dispersing group, neutralisation may not be required.

Preferably the base used to neutralise any anionic water-dispersing groups is ammonia, an amine or an inorganic base. Suitable amines include tertiary amines, for example triethylamine or triethanolamine. Suitable inorganic bases include alkaline hydroxides and carbonates, for example lithium hydroxide, sodium hydroxide, or potassium hydroxide. A quaternary ammonium hydroxide, for example  $N^+(CH_3)_4OH^-$ , can also be used. Generally a base is used which gives the required counter ion desired for the composition. For example, preferred counter ions include  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $NH_4^+$  and substituted ammonium salts.

Component (a) is preferably a hydrophilic acrylic, polyurethane or polyester polymer, more preferably a hydrophilic acrylic or polyurethane polymer, especially a hydrophilic polyurethane polymer.

When component (a) is a hydrophilic acrylic polymer it preferably has a glass transition temperature ( $T_g$ ) greater than  $-10^\circ C$  and more preferably from  $20^\circ C$  to  $120^\circ C$ .  $T_g$  is the temperature at which the polymer changes from a glassy, brittle state to a plastic, rubbery state, and may be measured by differential scanning calorimetry.

When component (a) is a hydrophilic acrylic polymer it preferably has an acid value from 30 to 200mgKOH/g, more preferably from 30 to 150mgKOH/g and especially from 40 to 100mgKOH/g.

The hydrophilic acrylic polymer has preferably been obtained from the polymerisation of one or more olefinically unsaturated monomers having ionic and/or non-ionic water-dispersing groups, optionally in the presence of one or more olefinically unsaturated monomers which are free from ionic and non-ionic water-dispersing groups.

Preferred olefinically unsaturated monomers having ionic water-dispersing groups include but are not limited to acrylic acid, methacrylic acid, itaconic acid,  $\beta$ -carboxy ethyl acrylate, maleic acid, monoalkyl itaconates (for example, monomethyl maleate, monoethyl maleate, monobutyl maleate and monoethyl maleate), citraconic acid, styrenesulfonic acid, vinylbenzylsulfonic acid, vinylsulfonic acid, acryloyloxyalkyl sulfonic acids (for example, acryloyloxymethyl sulfonic acid, acryloyloxyethyl sulfonic acid, acryloyloxypropyl sulfonic acid and acryloyloxybutyl sulfonic acid), methacryloyloxymethyl sulfonic acid, methacryloyloxyethyl sulfonic acid, methacryloyloxypropyl sulfonic acid and



methacryloyloxybutyl sulfonic acid), 2-acrylamido-2-alkylalkane sulfonic acids (for example, 2-acrylamido-2-methylethanesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid and 2-acrylamido-2-methylbutane sulfonic acid), 2-methacrylamido-2-alkylalkane sulfonic acids (for example, 2-methacrylamido-2-methylethanesulfonic acid, 2-methacrylamido-2-methylpropanesulfonic acid and 2-methacrylamido-2-methylbutanesulfonic acid), mono-(acryloyloxyalkyl)phosphates (for example, mono(acryloyloxyethyl)phosphate and mono(3-acryloyloxypropyl)phosphates) and mono(methacryloyloxyalkyl)phosphates (for example, mono(methacryloyloxyethyl)phosphate and mono(3-methacryloyloxypropyl)phosphate).

Especially preferred olefinically unsaturated monomers having ionic water-dispersing groups include acrylic acid, methacrylic acid, itaconic acid,  $\beta$ -carboxy ethyl acrylate, and / or maleic acid.

Preferred olefinically unsaturated monomers having non-ionic water-dispersing groups include alkoxy polyethylene glycol (meth)acrylates, preferably having a Mn of from 350 to 2000. Examples of such monomers which are commercially available include  $\omega$ -methoxypolyethylene glycol acrylate.

Preferred olefinically unsaturated monomers which are free from ionic or non-ionic water-dispersing groups include alkyl(meth)acrylates, optionally substituted styrenes, methacrylamides, pyrrolidones, and allyl compounds.

Preferred alkyl(meth)acrylates contain less than twenty carbon atoms. Examples include methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, sec-butyl acrylate, amyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, tert-octyl acrylate, 2-phenoxyethyl acrylate, 2-chloroethyl acrylate, 2-bromoethyl acrylate, 4-chlorobutyl acrylate, cyanoethyl acrylate, 2-acetoxyethyl acrylate, dimethylaminoethyl acrylate, benzyl acrylate, methoxybenzyl acrylate, 2-chlorocyclohexyl acrylate, acrylate, acetoacetate, cyclohexyl acrylate, furfuryl acrylate, tetrahydrofurfuryl acrylate, phenyl acrylate, 5-hydroxypentyl acrylate, 2,2-dimethyl-3-hydroxypropyl acrylate, 2-methoxyethyl acrylate, 3-methoxybutyl acrylate, 2-ethoxyethyl acrylate, 2-iso-propoxyethyl acrylate, 2-butoxyethyl acrylate, 2-(2-methoxyethoxy)ethyl acrylate, 2-(2-butoxyethoxy)ethyl acrylate, 1-bromo-2-methoxyethyl acrylate, 1,1-dichloro-2-ethoxyethyl acrylate, methyl methacrylate, ethyl methacrylate, hydroxyethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, sec-butyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzylmethacrylate, chlorobenzyl methacrylate, octyl methacrylate, N-ethyl-N-phenylaminoethyl methacrylate, 2-(3-phenylpropyloxy)ethyl methacrylate, dimethylaminophenoxyethyl methacrylate and furfuryl methacrylate. Aromatic examples include but are not limited to 4-alkyl phenylacrylate or methacrylate, phenyl methacrylate, phenyl acrylate, and  $\beta$ -naphthyl methacrylate.

Preferred optionally substituted styrenes include styrene, methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, diethylstyrene, isopropylstyrene,



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butylstyrene, hexylstyrene, cyclohexylstyrene, decylstyrene, chloromethylstyrene, trifluoromethylstyrene, ethoxymethylstyrene, acetoxymethylstyrene, methoxystyrene, 4-methoxy-3-methylstyrene, dimethoxystyrene, chlorostyrene, dichlorostyrene, trichlorostyrene, tetrachlorostyrene, pentachlorostyrene, bromostyrene, dibromostyrene, iodostyrene, trifluorostyrene and 2-bromo-4-trifluoromethylstyrene.

Preferred methacrylamides contain less than 12 carbon atoms. Examples include methylmethacrylamide, tert-butylmethacrylamide, tert-octylmethacrylamide, benzylmethacrylamide, cyclohexylmethacrylamide, phenylmethacrylamide, dimethylmethacrylamide, dipropylmethacrylamide, hydroxyethyl-N-methylmethacrylamide, N-methylphenylmethacrylamide, N-ethyl-N-phenylmethacrylamide and methacrylhydrazine.

Preferred allyl compounds include allyl acetate, allyl caprylate, allyl laurate, allyl palmitate, allyl stearate, allyl benzoate, allyl acetoacetate, allyl lactate, allyloxyethanol, allyl butyl ether and allyl phenyl ether.

The hydrophilic acrylic polymer may be prepared in a conventional manner by polymerising the olefinically unsaturated monomers having ionic and/or non-ionic water-dispersing groups, optionally in the presence of olefinically unsaturated monomers which are free from ionic and non-ionic water-dispersing groups. Temperatures from 20°C to 180°C are preferred. The polymerisation may be continued until reaction between the monomers is complete or the desired Mn has been reached.

Preferred polymerisation methods include solution polymerisation, emulsion polymerisation, suspension polymerisation and solution/dispersion polymerisation and such general methods as are well known in the art.

If desired, an initiator may be used to assist acrylic polymer formation. Suitable initiators include free-radical generators. Examples of initiators include azobis compounds, peroxides, hydroperoxides, redox catalysts, potassium persulfate, ammonium persulfate, tert-butyl peroctoate, benzoyl peroxide, isopropyl percarbonate, 2,4-dichlorobenzoyl peroxide, methyl ethyl ketone peroxide, cumene hydroperoxide, dicumyl peroxide, azobisisobutyronitrile, azobis(2-amidino-propane)hydrochloride and the like. Typically 0.05 to 5% by weight of initiator is used relative to the total weight of the monomers. Preferably the polymerisation is performed in the presence of an emulsifying agent.

Optionally the hydrophilic acrylic polymer is prepared by a process in which the Mn is controlled by the addition of chain transfer agents and/or through the adjustment of the ratio of the concentration of monomers relative to the concentration of initiator during the course of the polymerisation. Typical chain transfer agents are thiols, halocarbons and cobalt macrocycles.

When component (a) is a hydrophilic polyurethane the Mn is preferably less than 12,500, more preferably less than 10,000, especially less than 7,500 and more especially





less than 5,000. When component (a) is a hydrophilic polyurethane the Mn is preferably more than 500. Preferred hydrophilic polyurethanes are linear.

The hydrophilic polyurethane is preferably obtained from the reaction of at least one organic polyisocyanate and at least one isocyanate-reactive compound having ionic and/or non-ionic water-dispersing groups, optionally in the presence of isocyanate-reactive compounds which are free from ionic and non-ionic water-dispersing groups.

The organic polyisocyanate may be any known in the art, preferably having two isocyanate groups, and may for example be an aliphatic, cycloaliphatic, aromatic or araliphatic isocyanate. Examples of suitable organic polyisocyanates include ethylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, tetramethylxylene diisocyanate, 1,4-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenyl-methane diisocyanate and its hydrogenated derivative, 2,4'-diphenylmethane diisocyanate and its hydrogenated derivative, and 1,5-naphthylene diisocyanate. Mixtures of the polyisocyanates can be used, particularly isomeric mixtures of the toluene diisocyanates or isomeric mixtures of the diphenylmethane diisocyanates (or their hydrogenated derivatives), and also organic polyisocyanates which have been modified by the introduction of urethane, allophanate, urea, biuret, carbodiimide, uretonimine or isocyanurate residues.

Preferred organic polyisocyanates include cycloaliphatic polyisocyanates, especially isophorone diisocyanate, and aliphatic isocyanates, especially 1,6-hexamethylene diisocyanate or hydrogenated 4,4-diphenyl methyl diisocyanate.

The isocyanate-reactive compound preferably has at least one, more preferably two, isocyanate-reactive groups. Optionally isocyanate-reactive compounds having three isocyanate-reactive groups may be present, preferably in low levels not exceeding 5% by weight relative to the total weight of the isocyanate-reactive compound. Preferred isocyanate-reactive groups are selected from -OH, -NH<sub>2</sub>, -NH- and -SH. These isocyanate-reactive groups are capable of reacting with an isocyanate (-NCO) group.

Preferred isocyanate-reactive compounds having water-dispersing groups include low molecular weight polyols or polyamines bearing ionic and/or non-ionic water-dispersing groups. Preferred isocyanate-reactive compounds having anionic water-dispersing groups are diols having one or more sulphonic acid groups and/or carboxylic acid groups, more preferably dihydroxy alkanoic acids, especially 2,2-dimethylol propionic acid. Preferred isocyanate-reactive compounds having non-ionic water-dispersing groups are diols providing polyoxyethylene groups.

Preferred isocyanate-reactive compounds which are free from ionic and non-ionic water-dispersing groups include organic polyol(s) and / or polyamine(s). Preferred organic polyols or polyamines have a Mn up to 3000, more preferably up to 2000, especially from 400 to 2000. Preferred organic polyols are diols. The diols include members of any of the chemical classes of diols used or proposed to be used in polyurethane formulations. In particular, the diols are preferably polyesters, polyesteramides, polyethers (other than



ones providing polyoxyethylene groups), polythioethers, polycarbonates, polyacetals, polyolefins or polysiloxanes. Further examples of optional diols which are free from ionic and non-ionic water-dispersing groups include organic diols having an Mn below 400. Examples of such diols include ethylene glycol, diethylene glycol, tetraethylene glycol, bis(hydroxyethyl) terephthalate, cyclohexane dimethanol, and furan dimethanol.

The hydrophilic polyurethane may be prepared in a conventional manner by reacting one or more organic polyisocyanates with one or more isocyanate-reactive compounds. Substantially anhydrous conditions are preferred. Temperatures of from 30°C to 130°C are preferred and the reaction is preferably continued until the reaction between the organic polyisocyanates and the isocyanate-reactive compounds is substantially complete.

The relative amounts of the organic polyisocyanate and the isocyanate-reactive compounds are preferably selected such that the mole ratio of isocyanate groups to isocyanate-reactive groups is about 2:1 to 1:2, preferably from about 1.4:1 to 1:1.4. Alternatively an isocyanate-group terminated polyurethane prepolymer may be prepared in a two stage process either in solvent or as a melt, wherein the ratio of isocyanate groups to isocyanate-reactive groups is from about 1.1:1 to 2:1, preferably from about 1.1:1 to 1.9:1.

Terminating compounds, for example compounds having one isocyanate group or one isocyanate-reactive group, may be used to cap-off any excess isocyanate or isocyanate-reactive end groups in the polyurethane resulting from the reaction of the organic polyisocyanate and isocyanate-reactive compound. Compounds having one isocyanate-reactive group include, for example, monoalcohols, monoamines and monothiols, especially isopropanol. Compounds having one isocyanate reactive group include alkyl monoisocyanates. The Mn of the polyurethane may be controlled through the use of such terminating compounds. The terminating compounds may also bear ionic and/or non-ionic water-dispersing groups, for example the groups hereinbefore described.

If desired a catalyst may be used to assist formation of the hydrophilic polyurethane. Suitable catalysts include di-butyl tin dilaurate, stannous octoate and tertiary amines as known in the art.

Preferably the hydrophilic polyurethane is not prepared by chain-extension of an isocyanate-terminated polyurethane prepolymer (for example by mixing the hydrophilic polyurethane with water or water mixed with chain-extenders).

When component (a) is a hydrophilic polyester polymer, the Mn is preferably in the range from more than 500 to less than 30,000, more preferably in the range from 1000 to 25,000.

The Tg of the hydrophilic polyester is preferably in the range of from -38°C to 105°C.

The hydrophilic polyester is preferably obtained by polymerising at least one monomer having two or more functional groups which will readily undergo an ester



condensation reaction and having ionic and/or non-ionic water-dispersing groups, optionally in the presence of monomers having two or more functional groups which will readily undergo an ester condensation reaction which are free from ionic and non-ionic water-dispersing groups. Preferred anionic water-dispersing groups are as mentioned  
5 above, especially sulphonic acid groups, ionised sulphonate groups and carboxylic acid groups and ionised carboxyl groups.

Functional groups which will readily undergo an ester condensation reaction include carboxyl groups, hydroxyl groups and esterifiable derivatives thereof. Examples of such monomers are aromatic dicarboxylic acids having an ionised sulphonate group.  
10 Particularly preferred is sodio-5-sulphoisophthalic acid (SSIPa).

Other useful monomers which have two or more groups which readily undergo an ester condensation reaction and have one or more sulphonate groups are dihydroxy aryl monomers having at least one sulphonate group.

The amount of water-dispersing groups, for example ionised sulphonate and/or  
15 carboxy and/or non-ionic water-dispersing groups, present in the hydrophilic polyester is preferably sufficient to provide water-dissipatability of the polyester. Ionised sulphonate groups are more effective at providing or contributing to water-dissipatability than ionised carboxy groups and so can be used at considerably lower levels in comparison to ionised carboxy groups.

When the hydrophilic polyester mainly contains SSIPa as the monomer for  
20 providing the ionised sulphonate groups, the amount of this monomer used in the polyester synthesis, based on the weight of all the monomers used in the polyester synthesis, will usually be within the range from 5 to 20% by weight. The acid value of the hydrophilic polyester which contains mainly ionised sulphonate groups will generally be  
25 within the range of from 0 to 100 mgKOH/g, more preferably 0 to 50 mgKOH/g, especially 0 to 25 mgKOH/g, more especially 0 to 10mgKOH/g.

When the hydrophilic polyester predominantly contains ionised carboxy water-dispersing groups, the acid value of the polyester is preferably within the range of from 20 to 140 mgKOH/g more preferably 30 to 100 mgKOH/g.

30 Monomers having two or more functional groups which will readily undergo an ester condensation reaction and having non-ionic water-dispersing groups include mono-, di- or higher functional hydroxy compounds containing polyoxyethylene groups, for example polyethylene glycols and alkyl ethers of polyethylene glycols.

Monomers having two or more functional groups which will readily undergo an  
35 ester condensation reaction and are free from ionic and non-ionic water-dispersing groups include polybasic carboxylic acids and polyols in which the carboxylic acid groups and hydroxy groups are esterified during the polymerisation process. For example, aliphatic, alicyclic and aromatic compounds having two or more carboxy groups and their ester forming derivatives (e.g. esters, anhydrides and acid chlorides) may be used. Specific  
40 examples include adipic acid, fumaric acid, maleic acid, succinic acid, itaconic acid,



sebacic acid, nonanedioic acid, decanedioic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, terephthalic acid, isophthalic acid, phthalic acid and tetrahydrophthalic acid and their acid chlorides. Anhydrides include succinic, maleic, phthalic and hexahydrophthalic anhydrides.

5 Preferred polyols which can be used to form the polyester include those having from 2 to 6, more preferably 2 to 4 and especially 2 hydroxyl groups per molecule. Suitable polyols having two hydroxy groups per molecule include diols such as 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol (neopentyl glycol), the 1,2-, 1,3- and 1,4-cyclohexanediols and the corresponding  
10 cyclohexane dimethanols, diethylene glycol, dipropylene glycol, and diols such as alkoxylated bisphenol-A products, e.g. ethoxylated or propoxylated bisphenol A. Suitable polyols having three hydroxy groups per molecule include triols such as trimethylolpropane (1,1,1-tris (hydroxymethyl)ethane). Suitable polyols having four or more hydroxy groups per molecule include pentaerythritol (2,2-bis(hydroxymethyl)-1,3-propanediol) and sorbitol (1,2,3,4,5,6-hexahydroxyhexane).  
15

Preferably component (b) readily disperses in component (d). On dispersion the particle size of component (b) is preferably such that when present in the composition it has a particle size from 20 to 500nm, more preferably from 20 to 350nm, especially from 20 to 200nm. Particle size can be measured by, for example, laser light scattering  
20 electron microscopy.

Component (b) is preferably an hydrophobic acrylic or polyurethane polymer of Mn more than 40,000. The hydrophobic polymer is preferably prepared by the methods described above for the hydrophilic polymers, except that the ionic and non-ionic water-dispersing groups are omitted or are present in low amounts. Component (b) is preferably  
25 hydrophobic by virtue of being free from or having low levels of ionic and/or non-ionic water-dispersing groups. The hydrophobic polymer is preferably prepared by polymerising one or more monomers which are free from or having low levels of ionic and/or non-ionic water-dispersing groups. The level of monomers having water-dispersing groups is preferably from 0 to 25% by weight of the hydrophobic polymer.  
30 Although the hydrophobic polymer has only a low solubility in pure water, it is preferably chosen such that it does not precipitate out when in the composition of the invention.

When component (b) is a hydrophobic acrylic polymer the preferred acid value is from 0 to 30 mgKOH/g.

The Tg of the hydrophobic acrylic polymer is preferably in the range of from -10°C to 120°C, more preferably in the range of from 20°C to 110°C most preferably in the  
35 range of from 40°C to 110°C.

Preferably the hydrophobic acrylic polymer is a copolymer comprising styrene.

When component (b) is a hydrophobic polyurethane polymer, the hydrophobic polyurethane polymer can optionally be prepared by chain extending an isocyanate  
40 terminated polyurethane prepolymer, using techniques well known in the art. Suitable





chain extenders include polyols, amine alcohols, diamines, hydrazines, substituted hydrazines and water. When the chain extender is other than water, for example a diamine, it may be added to an aqueous dispersion of the polyurethane prepolymer or may already be present in the aqueous medium when the polyurethane prepolymer is dispersed therein. The hydrophobic polyurethane polymer may be linear, branched or crosslinked.

Component (a) and component (b) are optionally based on the same or different polymers. For example component (a) may be a hydrophilic polyurethane and component (b) a hydrophobic polyurethane or component (a) may be a hydrophilic polyurethane and component (b) may be a hydrophobic acrylic polymer, in each case having the Mn as specified above.

Components (a) and (b) optionally each comprise a mixture of polymers. For example component (a) may comprise a mixture of hydrophilic acrylic polymers or a mixture of a hydrophilic acrylic polymer and a hydrophilic polyurethane polymer.

In a preferred embodiment the polymers used as component (a) and component (b) in the composition of the invention are each independently selected from acrylic polymers and polyurethane polymers.

Components (a) and (b) are purified if desired in the usual way for colorants used in ink-jet printing inks, for example by ion-exchange, filtration, reverse osmosis, dialysis, ultra-filtration or a combination thereof. In this way one may remove co-solvents used for the polymerisation, low molecular weight salts, impurities and free monomers.

Components (a) and (b) can be combined in a number of ways. For example, components (a) and (b) can be prepared separately, followed by combination by blending. The blending may be performed at any stage, for example before components (a) and (b) are added to the liquid medium, or components (a) and (b) may be incorporated individually into the liquid medium and then blended. Alternatively, when component (a) is an acrylic polymer, components (a) and (b) can be combined by preparing component (b) by *in-situ* aqueous emulsion in the presence of component (a). When component (b) is an acrylic polymer, components (a) and (b) can be combined by preparing component (a) by an *in-situ* aqueous emulsion polymerisation in the presence of component (b). Preferably when components (a) and (b) are both acrylic polymers, components (a) and (b) are prepared separately, followed by combination by blending. When components (a) and (b) are both acrylic polymers and component (b) is prepared in the presence of component (a) then the Tg of component (b) is preferably greater than 40°C, more preferably greater than 45°C, most preferably greater than 50°C.

For example when component (b) is a hydrophobic acrylic polymer, the hydrophobic acrylic polymer may be prepared by aqueous polymerisation using component (a) (hydrophilic acrylic, polyurethane and/or polyester polymer) as a polymeric dispersant. Optionally additional surfactant may be used to aid dispersion. Preferably the aqueous polymerisation is carried out at a pH above 7.



Alternatively when component (b) is a hydrophobic acrylic polymer the hydrophobic acrylic polymer may be prepared by emulsion polymerisation at a low pH followed by *in-situ* polymerisation of a hydrophilic acrylic polymer component (a) at a low pH, with subsequent neutralisation with a base to pH 7.

5 The weight ratio of component (a) to component (b) is preferably from 5:95 to 99:1, more preferably from 5:95 to 95:5, especially from 5:95 to 50:50, more especially from 5:95 to 40:60, most especially of from 10:90 to 40:60.

10 In a preferred embodiment the weight ratio of component (a) to component (b) is from 99:1 to 50:50, preferably from 99:1 to 60:40, more preferably 99:5 to 60:40. This embodiment is preferred because compositions containing these ratios of components (a) to (b) perform particularly well in thermal ink-jet printers. Inks prepared from these compositions are stable, and prints prepared using the inks give a good performance in terms of wet rubfastness, light-fastness and highlighter smear resistance.

15 The pigment (component (c)) is preferably a water-insoluble colorant, preferably inorganic or organic. Preferred inorganic pigments include carbon black, titanium dioxide, zinc oxide, zirconium oxide, chromium oxide, iron oxide and combinations thereof.

20 Preferred organic pigments include phthalocyanine, anthraquinone, perinone, indigoid, perylene, azo, carbon black pigments carrying ionic groups, azomethine, condensed ring pigments and pigments as mentioned in the Colour Index International, Third Edition (1982) Pigments and Solvent dyes, pages 10 to 143, which are incorporated herein by reference thereto. Preferred organic pigments are yellows, reds, oranges, violets, blue and / or black. In particular it has been found that when using a coloured pigment the light-fastness of prints prepared using the inks is greatly improved. This improvement is particularly noticeable with coloured inorganic and/or organic pigments  
25 other than black pigments, for example yellow, red, orange, green, violet, indigo and blue pigments which tend to have lower light-fastness than black pigments.

30 The carbon black pigment optionally carries water-dispersing groups, especially ionic groups, for example anionic and/or cationic groups. The anionic groups preferably comprise a carboxylic, sulphonic or phosphonic acid group. The cationic groups preferably comprise a quaternary ammonium group. Carbon black pigments carrying ionic groups are commercially available from a number of sources, including Mitsubishi and Cabot corporation for example the Cabojet (Cabojet is a Trade Mark of Cabot) range of carbon black pigments. Particularly preferred is carbon black pigment having a mean particle size of from 5 to 100 nm, more preferably of from 10 to 30 nm. The carbon black  
35 pigment preferably has a pH of from 3 to 9.

The pigment used in the composition of the present invention is optionally a mixture comprising of two or more pigments. Pigments are present in any effective amount in the composition, typically from about 1 to about 10 percent by weight of the composition.



The liquid medium (component (d)) preferably comprises water and an organic solvent. The organic solvent preferably comprises a water-miscible organic solvent and/or a water-immiscible organic solvent.

Suitable water-miscible organic solvents include methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, isobutanol, dimethylformamide, dimethylacetamide, acetone, diacetone alcohol, tetrahydrofuran, dioxane, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol, diethylene glycol, thiodiglycol, polyethylene glycol, polypropylene glycol, glycerol, 1,2,6-hexanetriol, 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy) ethanol, 2-(2-butoxyethoxy)ethanol, 3-butoxypropan-1-ol, 2-[2-(2-methoxyethoxy)-ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]-ethanol, optionally substituted pyrrolidones, sulpholane and mixtures containing two or more of the aforementioned water-miscible organic solvents. Preferred water-miscible organic solvents are tetrahydrofuran, dioxane, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol, optionally substituted pyrrolidones, and sulpholane.

Suitable water-immiscible organic solvents include toluene, xylene, naphthalene, tetrahydronaphthalene, methyl naphthalene, chlorobenzene, fluorobenzene, chloronaphthalene, bromonaphthalene, butyl acetate, ethyl acetate, methyl benzoate, ethyl benzoate, benzyl benzoate, butyl benzoate, phenylethyl acetate, butyl lactate, benzyl lactate, diethyleneglycol dipropionate, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, di (2-ethylhexyl) phthalate, hexanol, octanol, benzyl alcohol, phenyl ethanol, phenoxy ethanol, phenoxy propanol, phenoxy butanol, anisole, phenetole, nitrocellulose, cellulose ether, cellulose acetate, low odour petroleum distillates, turpentine, white spirits, naphtha, isopropylbiphenyl, terpene, vegetable oil, mineral oil, essential oil, natural oil, C<sub>8</sub>-C<sub>12</sub> substituted pyrrolidones and mixtures of any two or more thereof. Benzyl alcohol is especially preferred.

The weight ratio of water-miscible organic solvent to water-immiscible organic solvent in the composition is preferably 19:1 to 1:1, more preferably 8:1 to 1:1, especially 5:1 to 1:1.

The compositions according to the present invention may be prepared by combining components (a), (b), (c) and (d) in any order. Suitable combining techniques are well known in the art, for example agitation, grinding, milling, ultrasonication or stirring of all the components. Preferably the composition is prepared by mixing components (a), (b), and (d) and optionally further components until the composition is homogenous. The mixture may then be added slowly with stirring to component (c) before adjusting the pH by addition of a base. Components (a), (b), (c) and (d) are preferably combined together under conditions which retain stability and avoid flocculation. The preferred pH range of the composition is of from 7 to 11, more preferably of from 9 to 10.

Preferably the composition comprises:



(i) from 0.1 to 10 parts, more preferably 1 to 5 parts, especially 2 to 4 parts of component (a);

(ii) from 0.1 to 10 parts, more preferably 1 to 10 parts, especially 2 to 9 parts, more especially 4 to 7 parts, of component (b);

5 (iii) from 0.1 to 15 parts, more preferably 2 to 10 parts, especially 4 to 8 parts of component (c); and

(iv) from 75 to 98 parts, more preferably 75 to 90 parts, especially 80 to 90 parts of component (d);

10 wherein all the parts are by weight and the parts by weight of (i) + (ii) + (iii) + (iv) add up to 100.

In addition to components (a), (b), (c) and (d), the composition optionally contains other components, such as a biocide, for example Proxel GXL (Proxel is a trade mark of Avecia Limited) or Kathon (Kathon is a trade mark of Rohm and Haas), a fungicide, a rheological agent, e.g. a wax (e.g. beeswax), a clay (e.g. bentonite), an IR absorber, or a  
15 fluorescent brightener, for example C.I. Fluorescent Brightener 179 and/or UV absorber, for example hydroxy phenylbenzotriazole. Furthermore the compositions optionally contain a surface active agent, wetting agent and/or an emulsifier, for example those described in McCutcheon's Emulsifiers and Detergents 1996 International Edition or in Surfactants Europa 3<sup>rd</sup> Edition 1996 each of which is incorporated herein by reference.

20 The viscosity of the composition is preferably less than 100cp, more preferably less than 50cp, especially less than 20cp, more especially less than 15cp and most preferably less than 10cp at 20°C.

25 Preferably the composition has been filtered through a filter having a mean pore size below 10 µm, preferably below 5 µm, more preferably below 2 µm, especially below 0.45 µm. In this way particulate matter is removed which could otherwise block fine nozzles in an ink-jet printer.

The composition preferably has a total concentration of divalent and trivalent metal ions below 5000, more preferably below 1000, especially below 100, more especially below 20 parts per million by weight relative to the total weight of the composition.

30 Pure compositions of this type may be prepared by using high purity ingredients and/or by purifying the composition after it has been prepared.

Suitable purification techniques are well known, for example ultrafiltration, reverse osmosis, ion exchange and combinations thereof.

35 In an embodiment of the present invention there is provided a composition comprising the components:

(a) a hydrophilic polymer having a number average molecular weight less than 30, 000;

(b) a hydrophobic polymer having a number average molecular weight more than 40,000;

40 (c) pigment; and





(d) liquid medium,  
wherein

- i) the composition has a viscosity less than 100 cp at 20°C;
- ii) the composition has been filtered through a filter having a mean pore size  
5 below 10  $\mu\text{m}$ ; and
- iii) the composition has a total concentration of divalent and trivalent metal ions  
below 5000 parts per million by weight relative to the total weight of the  
composition.

Preferably the composition is an ink, more preferably an ink suitable for use in an ink-jet  
10 printer.

The compositions according the invention have the advantage that they are  
suitable not only for the use in piezoelectric ink-jet printers but also in thermal and  
continuous ink-jet printers. Such compositions form discrete droplets on the substrate  
with little tendency for diffusing. Consequently sharp images with excellent print quality  
15 and little if any bleed between colours printed side by side can be obtained. Furthermore  
the compositions show good storage stability, wet and light fastness and fastness to both  
acidic and alkaline highlighter pens.

A third aspect of the invention provides a process for printing an image on a  
substrate comprising applying thereto a composition comprising the components

- 20 (a) a hydrophilic polymer having a number average molecular weight less than  
30,000;
- (b) a hydrophobic polymer having a number average molecular weight more  
than 40,000;
- (c) pigment; and
- 25 (d) liquid medium.

by means of an ink-jet printer.

The ink-jet printer preferably applies the composition to the substrate in the form of  
droplets which are ejected through a small nozzle onto the substrate. Preferred ink-jet  
printers are piezoelectric ink-jet printers and thermal ink-jet printers. In thermal ink-jet  
30 printers, programmed pulses of heat are applied to the compositions in a reservoir by  
means of a resistor adjacent to the nozzle, thereby causing the compositions to be ejected  
in the form of small droplets directed towards the substrate during relative movement  
between the substrate and the nozzle. In piezoelectric ink-jet printers the oscillation of a  
small crystal causes ejection of the compositions from the nozzle.

35 The substrate is preferably a paper, plastic, or textile material, more preferably a  
paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain, coated or treated papers which may have an acid,  
alkaline or neutral character. Most preferably the substrate is a coated paper.

According to a further feature of the invention there is provided an ink-jet printer  
40 cartridge, optionally refillable, containing a composition as hereinbefore defined.



The invention will now be described by example only. All parts and percentages are by weight unless specified otherwise. CI refers to pigments as mentioned in the Colour Index International Third Edition (1982).

#### Preparation of Polymer Composition 1

5 Polymer Composition 1 comprises component 1(a) and component 1(b) where component 1(b) is prepared by an *in-situ* emulsion polymerisation in the presence of component 1(a) where the ratio of component 1(a) to component 1(b) is 35:65 w/w.

#### Stage 1 - Preparation of component 1(a):

10 Component 1(a) is a hydrophilic acrylic copolymer of Mn less than 30,000, with a composition of MAA/MMA/BA (10/69.5/20.5), prepared by an emulsion polymerisation using material as listed below in Table 1:

Table 1

	Materials	Weight (g)	Percentage
	De-ionised Water	436.5	32.82
<u>monomer shot</u>	Methyl methacrylate	25.9	1.9
	Butyl acrylate	7.6	0.6
	3 Mercaptopropionic acid	1.1	0.08
<u>monomer feed</u>	Methacrylic acid (MAA)	37.4	2.8
	Methyl methacrylate (MMA)	233.7	17.6
	Butyl acrylate (BA)	68.8	5.2
	3-Mercaptopropionic acid	10.0	0.7
<u>initiator shot</u>	Ammonium persulphate	0.4	0.03
	De-ionised water	12.0	0.9
	Sodium lauryl sulphate	0.6	0.04
<u>initiator feed</u>	Ammonium persulphate	3.3	0.25
	De-ionised water	108.5	8.16
	Sodium lauryl sulphate	5.0	0.4
<u>burn-up</u>	Ascorbic acid	2.24	0.17
<u>co-initiator</u>	De-ionised water	42.58	3.20
<u>burn-up</u>	t-Butyl hydrogen peroxide	3.20	0.24
<u>initiator</u>	De-ionised water	41.62	3.13
<u>odour reducer</u>	Hydrogen peroxide solution 30%	2.49	0.19
	De-ionised water to take up to 30% solids	2.50	18.50
<u>neutralisation</u>	Ammonia solution 20%	36.91	2.78



Water was added to a reactor and heated to 80°C with continuous stirring. The reactor was purged with N<sub>2</sub>.

The monomer shot was added to the reactor and stirred for 5 minutes. The initiator shot was added to seed the reaction and stirred for 15 minutes. Monomer and initiator feeds were then added over 90 minutes whilst maintaining the temperature at 80-83°C for a further hour.

Subsequently the emulsion was cooled to 50°C to commence burn-up by adding the burn-up co-initiator dropwise over 30 minutes. The burn-up initiator was added in 3 equal shots at 1, 10 and 20 minutes of the burn-up co-initiator addition.

The mixture was stirred for 30 minutes before adding the hydrogen peroxide solution dropwise over 10 minutes. De-ionised water was added to take the emulsion to 30% solids w/w and the temperature increased to 60°C.

The emulsion was then neutralised with ammonia solution and stirred until the solution had gone clear. The resultant hydrophilic polymer was cooled and filtered through a 50µm mesh.

#### Analysis

The resultant hydrophilic polymer solution (component 1(a)) had a pH of 7.0, a weight average molecular weight (Mw) of 13289 and an Mn of 5,446. The Tg average was 66°C.

#### Stage 2 - Preparation of component 1(b):

Component 1(b) is a hydrophobic acrylic homopolymer of Mn more than 40,000, comprising styrene. Preparation of component 1(b) is carried out by an *in-situ* emulsion polymerisation of the materials as listed in Table 2 below, in the presence of component 1(a) as prepared in stage 1 above.

Table 2

	Materials	Weight (g)	Percentage
<u>initial charge</u>	Product from stage 1.	386.68	34.40
	De-ionised water	379.77	33.79
	Ammonia solution 35%	10.0	0.89
<u>emulsified feed</u>	Styrene (STY)	217.74	19.37
	De-ionised water	108.88	9.69
	Ammonium persulphate	1.09	0.1
	Sodium lauryl sulphate	1.09	0.1
	De-ionised water for rinse	18.75	1.69



The initial charge was added to a reactor with enough ammonia solution to ensure that the pH of the initial charge was greater than 8.5, and heated to 80-85°C with continuous stirring under nitrogen.

10% of the emulsified feed was added to the reactor from a dropping funnel and left to nucleate for about 5 minutes. After nucleation the remainder of the emulsified feed was added over an hour while the temperature of  $85 \pm 2^\circ\text{C}$  was maintained. Once all the feed was added the dropping funnel was rinsed with de-ionised water which was subsequently added to the reactor. The reaction was left for a further 30 minutes at 85°C before cooling the resultant composition to room temperature and filtering the composition through a 50µm mesh.

The resultant Polymer Composition 1 was made up to 30 % solids w/w with deionised water, had a pH of 8.8, a particle size of 38 nm and the Mn of component 1(b) was 214,000.

#### Preparation of Polymer Composition 2

Polymer Composition 2 comprises a blend of component 2(a) with component 2(b) where the ratio of component 2(a) to component 2(b) is 42:58.

#### Stage 1 - Preparation of component 2(a):

Component 2(a) is a hydrophilic acrylic copolymer of Mn less than 30,000, with a composition of MAA/MMA (10/90) prepared by an emulsion polymerisation.

The method described above for the preparation of polymer composition 1, stage 1 was repeated except that the monomer shot and monomer feed were as described in Table 3 below.

Table 3

	Materials	<u>weight (g)</u>
<u>monomer shot</u>	methyl methacrylate	33.7
	3-mercaptopropionic acid	1.1
<u>monomer feed</u>	methacrylic acid	37.4
	methyl methacrylate	302.9
	3-mercaptopropionic acid	10.0

#### Analysis

The resultant hydrophilic polymer solution had a solids content of 30% solids w/w, a pH of 7.0 and a Mn of 5541.

#### Stage 2 - Preparation of component 2(b):





Component 2(b) is a hydrophobic acrylic copolymer of Mn more than 40,000, with a composition of SY/AA (96/4) prepared by an emulsion polymerisation, with materials as listed in Table 4 below.

Table 4

	Materials	Weight (g)	Percentage
<u>monomer shot</u>	De-ionised water	442.2	33.95
	Styrene	48	3.7
	Acrylic acid	2	0.15
<u>monomer feed</u>	Styrene	432	33.2
	Acrylic acid	18	1.4
<u>initiator shot</u>	Ammonium persulphate	0.25	0.02
	Sodium lauryl sulphate	1.0	0.08
	De-ionised water	13.1	1.0
<u>initiator feed</u>	Ammonium persulphate	2.25	0.17
	Sodium lauryl sulphate	9.0	0.7
	De-ionised water	117.8	9.0
<u>burn-up co-initiator</u>	Ascorbic acid	1.5	0.12
	De-ionised water	28.5	2.19
<u>burn-up initiator</u>	t-Butyl hydrogen peroxide	2.14	0.16
	De-ionised water	27.86	2.14
<u>neutralisation</u>	De-ionised water	143.37	11.01
	Ammonia solution 35%	13.5	1.04

Water was added to a reactor and heated to 80°C with continuous stirring. The reactor was purged with N<sub>2</sub>.

The monomer shot was added to the reactor and stirred for 5 minutes. The initiator shot was added to seed the reaction and stirred for 15 minutes. Monomer and initiator feeds were then added over 90 minutes whilst maintaining the temperature at 80-83°C for a further hour.

Subsequently the emulsion was cooled to 50°C to commence burn-up by adding the burn-up co-initiator dropwise over 30 minutes. The burn-up initiator was added in 3 equal shots at 1, 10 and 20 minutes of the burn-up co-initiator addition.

The mixture was stirred for 30 minutes before adding the hydrogen peroxide solution dropwise over 10 minutes. De-ionised water was added to take the emulsion to 30% solids w/w and the temperature increased to 60°C.



The emulsion was then neutralised with ammonia solution and stirred until the mixture had gone clear. The resultant hydrophobic polymer emulsion was cooled and filtered through a 50µm mesh.

#### Analysis

The resultant hydrophobic polymer emulsion, component 2(b), had a pH of 9.6, an average particle size of 94 nm, and an Mn of 80,195.

#### Stage 3 - Preparation of a blend of components 2(a) and 2(b)

Component 2(a) from stage 1 (28g) was added to component 2(b) from stage 2 (39g), mixed thoroughly and de-ionised water was added to take the emulsion to 30% solids w/w to give Polymer Composition 2.

#### Preparation of Polymer Compositions 3, 4 & 5

Polymer Compositions 3, 4 & 5 comprise blends of component 3(a) with component 3(b) where for:

Polymer Composition 3 the ratio of component 3(a) to component 3(b) is 90:10, for Polymer Composition 4 the ratio of component 3(a) to component 3(b) is 80:20, and for Polymer Composition 5 the ratio of component 3(a) to component 3(b) is 70:30. Polymer Composition 5 the ratio of component 3(a) to component 3(b) is 25:70.

#### Stage I - Preparation of component 3(a)

Component 3(a) is a hydrophilic polyurethane polymer of Mn less than 30,000 with materials as listed below in Table 5.

Table 5

	Materials	Weight (g)
1.	Dimethylol propionic acid (DMPA)	6
2.	1,4-Cyclohexane dimethanol (CHDM)	5.25
3.	Polypropylene glycol 1000 (PPG)	27.5
4.	Isophorone diisocyanate (IPDI)	36.2
5.	Dibutyl tin dilaurate (DBTDL)	0.08
6.	N-methyl-2-pyrrolidinone (NMP)	18.7
7.	Jeffamine M1000	112
8.	Ammonia (35% solution)	1.4
9.	De-ionised water	546

#### Procedure

Materials 1, 2, 3, and 4 were added to a reactor and stirred under N<sub>2</sub>. Material 5 was added to the reactor and heated to 50°C with continuous stirring under N<sub>2</sub>. Dibutyl tin dilaurate was added to the reactor and heated to 90°C for three hours before removing a sample for isocyanate content determination. This was repeated until the isocyanate



content (NCO) had reached 4.66%, after which Jeffamine M1000 is added to the reactor and stirred for one hour at 90°C. The reaction mixture is dispersed into a mixture of ammonia (35%) and de-ionised water and stirred for one hour at room temperature, before filtering the dispersion through a 50µm mesh. Further de-ionised water was added to take the emulsion to 10% solids w/w.

Analysis: The resultant hydrophilic polymer emulsion, component 3(a) had a pH of 8.8, a weight average molecular weight of 7189, an Mn of 4621 and a viscosity at 10% solids w/w of 2.56 cps.

Stage 2 - component 3(b):

Component 3(b) is a commercially available polyurethane dispersion R985 NeoRez, available from NeoResins, Avecia b.v. with a Mn > 50,000, which was combined with de-ionised water to take the dispersion to 10% solids w/w. (NeoRez and NeoResins are trade marks of Avecia B.V).

Stage 3 - Preparation of blends of components 3(a) and 3(b):

Component 3(a) from stage 1 and component 3(b) from stage 2 were mixed thoroughly to give three blends, each having a solids content of 10% solids w/w. The quantities of components 3(a) and 3(b) used for each blend are listed below in Table 6.

Table 6

Polymer Composition	component 3(a) weight (g)	component 3(b) weight (g)	ratio (a):(b)
3	90	10	90:10
4	80	20	80:20
5	70	30	70:30
6	25	75	25:75

Preparation of Inks:

Example 1 and Example 2:

The materials listed below in Table 7 were mixed until homogeneous, and then the pH was adjusted to approximately 9.5 by the addition of 35% ammonia solution. To remove any particulate matter, the resultant emulsion was subsequently filtered through a 0.10 µm mesh.

Comparative Examples 1, 2 and 3:

Comparative Examples 1, 2 and 3 were prepared as described above for Example 1, where Comparative Example 1 contains no components (a) or (b), Comparative Example 2 only contains component 2(a) and Comparative Example 3 only contains component 2(b).



Table 7

Materials (%)	Examples		Comparative Examples		
	1	2	1	2	3
Cabojet 300 <sup>x</sup>	26	26	26	26	26
Diethylene glycol	10	10	10	10	10
Urea	5	5	5	5	5
Butyl Digol	2	2	2	2	2
Surfynol 465	0.1	0.1	0.1	0.1	0.1
Polymer Composition 1 components 1(a) and 1(b)	33.3	-	-	-	-
Polymer Composition 2 components 2(a) and 2(b)	-	33.2	-	-	-
component 2(a) only	-	-	-	33.3	-
component 2(b) only	-	-	-	-	33.3
De-ionised water	23.6	23.6	23.6	23.6	23.6
x = Cabojet 300 is at 15.3% solids w/w in de-ionised water					

Example 3, 4, 5 and 6

- 5 The materials listed below in Table 8 were mixed until homogeneous, and then the pH was adjusted to approximately 9.5 by the addition of 2-amino-2-methyl propanol. To remove any particulate matter, the resultant emulsion was subsequently filtered through a 0.45  $\mu$ m mesh.

Comparative Examples 4 and 5:

- 10 Comparative Examples 4 and 5 were prepared as described above for Example 3, where Comparative Example 4 only contains component 3(a) and Comparative Example 5 only contains component 3(b).





Table 8

Materials (%)	Examples				Comparative Examples	
	3	4	5	6	4	5
Cabot Carbon IJX157B	4.5	4.5	4.5	4.5	4.5	4.5
Polymer Composition 3 (3(a):3(b)=90:10)	9.0	-	-	-	-	-
Polymer Composition 4 (3(a):3(b)=80:20)	-	9.0	-	-	-	-
Polymer Composition 5 (3(a):3(b)=70:30)	-	-	9.0	-	-	-
Polymer Composition 6 (3(a):3(b)=25:75)	-	-	-	9.0	-	-
Component 3(a)	-	-	-	-	9.0	-
Component 3(b)	-	-	-	-	-	9.0
Diethylene glycol	10	10	10	10	10	10
Pentanediol	5.0	5.0	5.0	5.0	5.0	5.0
Proxel GXL (biocide - Avecia Ltd)	0.1	0.1	0.1	0.1	0.1	0.1
Surfynol 465 (surfactant - Air Products)	0.2	0.2	0.2	0.2	0.2	0.2
De-ionised water	71.2	71.2	71.2	71.2	71.2	71.2

#### Evaluation of the inks prepared in Examples 1 to 6 and Comparative Examples 1 to 5

5           The inks prepared in Examples 1 and 2, and Comparative Examples 1, 2 and 3 were evaluated for stability and were fired from an Epson 600 piezo ink-jet printer onto Conqueror High White Wove 100g/m<sup>2</sup> plain paper from Arjo Wiggins Ltd.

10           The inks prepared in Examples 3, 4, 5 and 6 and Comparative Examples 4 and 5 were evaluated for stability and were fired from a Hewlet Packard HP690C thermal ink-jet printer onto Xerox 4024 DP paper. The resultant prints were evaluated for highlighter smear resistance, print quality and wet rubfastness. The evaluation test results are shown below in Table 9.



Table 9

Example	Polymer	Ink stability data				Printed ink performance			
		RT	60° C	70° C	TC	Wet rub fastness	Highlighter smear	Print Quality	OD
1	Polymer Composition 1 Components 1(a) and 1(b) [35:65]	5	5	2	5	very little smear	no smear 100%	good	-
2	Polymer Composition 2 Components 2(a) and 2(b) [42:58]	5	5	5	5	very little smear	no smear 100%	good	-
3	Polymer Composition 3 Components 3(a) and 3(b) [50:10]	5	-	-	-	little smear	little smear	good	-
4	Polymer Composition 4 Components (3a) and 3(b) [80:20]	5	-	-	-	very little smear	very little smear	good	-
5	Polymer Composition 5 Components 3(a) and 3(b) [70:30]	5	-	-	-	no smear	no smear	good	-
6	Polymer Composition 6 Components 3(a) and (3b) [25:75]	5	-	-	4 (8weeks)	little smear	very little smear	good	0.97
CE 1	No polymers	5	5	5	5	smear	smear	very poor	-
CE2	Component 2 (a) only	1	1	1	1	did not print	did not print	did not print	-
CE3	Component 2 (b) only	5	5	5	5	did not print	did not print	did not print	-
CE4	Component 3 (a) only	5	-	-	-	smear	smear	good	0.92
CE5	Component 3 (b) only	5	-	-	-	did not print	did not print	very poor	-

KEY:-

- = Not measured
- CE = Comparative example
- RT = room temperature
- TC = Temperature cycle
- OD = Optical density



#### Highlighter smear resistance

This is a test performed 5 minutes after printing.

A yellow highlighter pen was used to draw a horizontal line across a series of printed vertical bars. The amount of ink smear between the vertical bars was assessed visually against controls.

#### Wet rubfastness

This is a test performed 5 minutes after printing.

A finger was wetted and rubbed on the corner of a printed solid black block. The amount of ink transferred to white paper is assessed visually against controls.

#### Ink Stability

The ink resulting from stage 1 were stored in an incubator at a range of temperatures for one week or eight weeks, as stated with the results. The temperature cycle was a 24 hour cycle (-10°C to 25°C).

The stability was evaluated by optical microscopy and the stability was ranked as follows:

Rank	Description
5	No change, good mobile dispersion
4	Good, a few 1 micron particles present, still mobile
3	An increase in the amount of particles greater than 1 micron
2	Large (greater than 2 micron) flocculates present, ink less mobile
1	Flocculated, immobile, unstable

#### Optical Density

The optical density is a measure of the colour strength of a printed image and is expressed as a number without units. The higher the value, the stronger the print is. Optical density is measured using an X-Rite 938 Spectrodensitometer.

#### Print Quality

The print quality is a subjective microscopic evaluation of the print edge quality and the uniformity of dot spread where a non-uniform dot spread includes wicking and feathering.

#### Preparation of pigment millbases for use in Examples 7, 8 and 9:

Pigment millbases were prepared by milling the materials as shown below in Table 10.



Materials (parts by weight)	Examples			Comparative Examples		
	7	8	9	6	7	8
Polymer Composition 1	6	6	6	-	-	-
Pigment Millbase 1*	20	-	-	20	-	-
Pigment Millbase 2*	-	20	-	-	20	-
Pigment Millbase 3*	-	-	20	-	-	20
Diethylene glycol	10	10	10	10	10	10
Pentane diol	-	-	-	5	5	5
Urea	5	5	5	-	-	-
Butyldigol	2	2	2	-	-	-
Surfynol 465	0.1	0.1	0.1	-	-	-
De-ionised water	72.9	72.9	72.9	81	81	81

\* = equivalent to 4 parts by weight of pigment





Evaluation of the inks prepared in Examples 7, 8 and 9 and Comparative Examples 6, 7 and 8

The inks prepared in Examples 7, 8 and 9 and Comparative Examples 6, 7 and 8 were fired from an Epson 660 piezo ink-jet printer onto Seiko Epson (SEC) glossy film, glossy paper and coated paper. The resultant prints were evaluated for light-fastness by measurement of the  $\Delta E$  after 100 hours in an Atlas Weatherometer. The evaluation test results are shown below in Table 12. The lower the value of  $\Delta E$ , the better the light fastness.

Table 12

	Lightfastness $\Delta E$ after 100 hours		
	SEC glossy film	SEC glossy paper	SEC coated paper
Example 7	20.79	-	-
Comparative Example 6	66.85	-	-
Example 8	1.19	1.05	0.69
Comparative Example 7	3.19	1.95	2.95
Example 9	2.99	2.99	-
Comparative Example 8	7.39	7.39	-
- = not measured			

From Table 12 it can be seen that Examples 6, 7 and 8 which contain Polymer Composition 1 have significantly better light-fastness than Comparative Examples 6, 7 and 8.

Preparation of Polymer Compositions 7, 8 and 9:

Polymer Compositions 7, 8 and 9 comprise components (a) and (b) where component (b) is prepared by an *in-situ* emulsion polymerisation in the presence of component (a) where the ratio of component (a) to component (b) is 35:35 w/w.

Polymer Composition 7 = component 1(a) and component 4(b)

Polymer Composition 8 = component 1(a) and component 5(b)

Polymer Composition 9 = component 1(a) and component 6(b)

Components 4(b), 5(b) and 6(b) are hydrophobic acrylic polymers prepared by an *in-situ* emulsion polymerisation in the presence of component 1(a) using the method described for the preparation of component 1(b) in the presence of component 1(a) and the monomers used for components 4(b), 5(b) and 6(b) are as listed below in Table 13.



Table 13

	Monomers w/w		Mn	Mw	Calculated T <sub>g</sub> °C
	Styrene	2-hydroxyethyl acrylate			
Component 4(b)	100	0	303996	763892	100
Component 5(b)	67	33	356847	976456	32
Component 6(b)	31	69	316677	1022088	-19

Preparation of inks:Examples 10, 11 and 12

- 5 The inks were prepared and fired as described for Example 3 above and the evaluation test results are shown below in Table 14.

Table 14

Example	Polymer	Ink Stability Data			Print Quality	Wet rub fastness
		room temperature	70 °C 1 week	OD		
10	Polymer composition 7 Components 1(a) and 4(b)	5	4	1.09	very good	very good
11	Polymer composition 8 Components 1(a) and 5(b)	5	4	1	good	very good
12	Polymer composition 9 Components 1(a) and 6(b)	5	4	1.03	adequate	very good

- 10 From Table 14 it can be seen that examples 10 and 11 in which components 4(b) and (5b) respectively have a T<sub>g</sub> above 20°C have a better print quality than Example 12, although all three examples show a very good wet rub fastness.

Preparation of Polymer Compositions 10 to 16

- 15 Polymer compositions 10 to 16 comprise blends of components (a) with component (b) where the ratio of component (a) to component (b) is 25:75 w/w.  
 Polymer Composition 10 = component 4(a) and component 3(b)  
 Polymer Composition 11 = component 4(a) and component 7(b)  
 Polymer Composition 12 = component 5(a) and component 3(b)



Polymer Composition 13 = component 5(a) and component 7(b)

Polymer Composition 14 = component 1(a) and component 8(b)

Polymer Composition 15 = component 4(a) and component 2(b)

- 5 Components 4(a) and 5(a) are hydrophilic polyurethane polymers prepared using the method described above for component 3(b) with materials and analysis results as listed below in Table 15.

Table 15

	Component 4(a)	Component 5(a)
Materials	Weight (g)	Weight (g)
1. DMPA	3.0	0
2. CHDM	8.25	11.25
3. PPG 1000	27.9	28.3
4. IPDI	35.8	35.45
5. DBTDL	0.08	0.08
6. NMP	19	19
7. Jeffamine M 1000	115.26	108.41
8. Ammonia 35% sol	1.4	0
9. De-ionised Water	546	528
Analysis		
Solids content	24.1%	23.9%
Mn	4343	4986
Mw	6676	7529
Viscosity at 10% solids (spindle 0 at 60 rpm)	2.47	2.35

10

Components 7(b) and 8(b) are commercially available dispersions from NeoResins, Avecia BV.

15

Component 7(b) is NeoRez R2001, an aliphatic modified polyurethane dispersion, with a Mn >50,000. Component 8(b) is NeoRez 970, an aliphatic polyether polyurethane dispersion with a Mn > 50,000. Each component 7(b) and 8(b) was combined with deionised water to take the dispersion to 10% solids w/w. (NeoRez and NeoResins are trade marks of Avecia BV).



Preparation of Inks

Examples 13 to 18 and Comparative Examples 9 to 12.

Inks were prepared, evaluated for stability and fired as described for Example 3 and Comparative Example 4 above and the evaluation test results are shown below in Table 16.





TABLE 16

Example	Polymer Composition	Ink Stability 8 weeks at 60°C	Print Quality	Wet Fastness	Highlighter Smear	O.D.
13	Polymer Composition 10 [Component 4(a) and 3(b)]	4	Good	Little Smear	No smear	0.98
14	Polymer Composition 11 [Component 4(a) and 7(b)]	4	Good	Very little smear	No smear	0.98
15	Polymer Composition 12 [Component 5(a) and (3b)]	4	Good	Very little smear	No smear	0.98
16	Polymer Composition 13 [Component 5(b) and 7(b)]	4	Good	Little Smear	No smear	0.98
17	Polymer Composition 14 [Component 1(a) and 8(b)]	4	Adequate	Little smear	No smear	0.94
18	Polymer Composition 15 [Component 4(a) and 2(b)]	4	Good	Very little smear	Little smear	0.98
Comparative Example						
9	Component 4(a)	4	Good	Little smear	Little smear	0.92
10	Component 7(b)	1	Good	Very little smear	Little smear	1.0
11	Component 5(a)	4	Poor	Little smear	Some smear	0.92
12	Component 8(b)	3	Poor	Smear	No smear	0.84



CLAIMS

1. A composition comprising the components:
  - (a) a hydrophilic polymer having a number average molecular weight less than 30,000;
  - (b) a hydrophobic polymer having a number average molecular weight more than 40,000;
  - (c) pigment; and
  - (d) liquid medium.
2. A composition according to claim 1 wherein component (a) has a number average molecular weight less than 20,000.
3. A composition according to claim 1 wherein component (b) has a number average molecular weight greater than 60,000.
4. A composition according to claim 1 wherein component (a) and component (b) are each independently selected from the group consisting of acrylic polymers, polyurethanes and polyesters.
5. A composition according to any one of the preceding claims wherein the hydrophobic polymer comprises a hydrophobic acrylic polymer and a hydrophobic polyurethane polymer.
6. An composition according to any one of the preceding claims wherein the hydrophilic polymer is hydrophilic by virtue of the presence of ionic and/or non-ionic water dispersing groups in the hydrophilic polymer.
7. A composition according to any one of the preceding claims wherein the composition has a total concentration of divalent and trivalent metal ions below 5000 parts per million by weight relative to the total weight of the composition.
8. A composition according to any one of the preceding claims having a viscosity less than 100cp at 20 °C.
9. A composition according to any one of the preceding claims wherein
  - (i) the composition has a viscosity less than 100 cp at 20°C;
  - (ii) the composition has been filtered through a filter having a mean pore size below 10µm; and
  - (iii) the composition has a total concentration of divalent and trivalent metal ions



below 5000 parts per million by weight relative to the total weight of the composition.

10. A composition according to any one of the preceding claims which comprises:

- (i) from 0.1 to 10 parts of component (a);
- (ii) from 0.1 to 10 parts, more preferably 1 to 10 parts of component (b);
- (iii) from 0.1 to 15 parts of component (c); and
- (iv) from 75 to 98 parts of component (d)

wherein all the parts are by weight and the parts by weight of (i) + (ii) + (iii) + (iv) add up to 100.

11. A composition according to any one of the preceding claims wherein the pigment is selected from yellow, red, orange, green, violet, indigo, blue and/or black organic and/or inorganic pigment.

12. A composition according to any one of the preceding claims wherein the pigment is a carbon black pigment.

13. A composition according to claim 12 wherein the carbon black pigment carries ionic groups.

14. A composition according to claim 1 with the proviso that when components (a) and (b) are both acrylic polymers, components (a) and (b) have been prepared separately.

15. A composition according to claim 1 with the proviso that when components (a) and (b) are both acrylic polymers and component (b) is prepared in the presence of component (a) then the Tg of component (b) is greater than 40°C.

16. A composition according to claim 15 where the Tg of component (b) is greater than 45°C.

17. An ink comprising a composition according to any one of the preceding claims.

18. Use of a composition according to claims 1 to 16 as an ink for ink-jet printing.

19. A process for printing an image on a substrate comprising applying thereto composition according to any one of claims 1 to 16 by means of an ink-jet printer.

20. An ink-jet printer cartridge containing a composition according to any one of claims 1 to 16.



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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/00703

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 822 238 A (DU PONT) 4 February 1998 (1998-02-04) page 3, line 30-57 page 4, line 6-29 page 4, line 30 -page 5, line 19 page 5, line 35-40	1,10-13, 17-20
A	US 4 925 885 A (ROSTHAUSER JAMES W ET AL) 15 May 1990 (1990-05-15) column 11, line 38-41; claims 1-3	1,10
A	EP 0 796 901 A (TOYO INK MFG CO) 24 September 1997 (1997-09-24) cited in the application	

☐ Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
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**INTERNATIONAL SEARCH REPORT**

information on patent family members

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(54) **Ink jet recording liquid**

(57) The present invention relates to an aqueous ink jet recording liquid of a pigment type, which liquid has excellent stability and printing characteristics; and also to a process for the preparation of said liquid. The ink jet recording liquid of the present invention is obtained by dispersing a pigment and a resin in an aqueous medium. Said resin is an aqueous dispersion-type resin comprising a shell composed of a polymer having a glass transition point in the range of 50° C to 150° C and a core composed of a polymer having a glass transition point in the range of -100° C to 40° C.

**EP 0 796 901 A2**

## Description

### BACKGROUND OF THE INVENTION

#### 5 Field of the Invention

The present invention relates to an ink jet recording liquid. More specifically, this invention relates to an aqueous ink jet recording liquid containing pigment, having excellent dispersion stability and printing characteristics; and also the process for preparing the liquid.

#### 10 Description of the Prior Art

Various aqueous ink jet recording liquids have been in use which are prepared by dissolving water-soluble dyes in aqueous media and adding variety of additives as needed to the resulting solutions. Particularly important properties required for such an aqueous ink jet recording liquid are as follows:

- (1) ability to produce high-quality recording images free from bleeding,
- (2) rapid drying and fixing rate of the recording liquid,
- (3) the recording liquid can be discharged stably without causing clogging of the recording liquid at a nozzle and liquid flow passages,
- (4) a superior storage stability of the recording liquid,
- (5) a high recording density, and
- (6) a superior weather- and water-resistance of the printed matter.

25 To impart stability to a recording liquid, acid dyes, direct dyes or basic dyes have been customarily used for the ink jet recording liquid as disclosed in Japanese Patent Application Laid-Open No. S53-61412, S54-89811, S55-65269 or the like. Those dyes, however, are accompanied by the problem of poor water resistance because of their high water-solubility. Moreover, weather resistance of dyes is generally poor.

In order to improve such poor water resistance, there have been attempts to structurally alter a dye and/or prepare a strongly basic recording liquid as disclosed in Japanese Patent Application Laid-Open No. S56-57862.

30 There have also been attempts to improve the water resistance by making use of the reaction between the recording paper and the recording liquid as disclosed in Japanese Patent Application Laid-Open No. S50-49004, S57-36692, S59-20696, and S59-146889.

The above-described attempts have produced desired results in certain types of recording paper. The recording liquid using a water-soluble dye, however, does not impart sufficient water resistance to the recorded material because of a large variety of recording paper used in ink jet printing. In addition, it is accompanied by bleeding of recorded images and slow drying rate of the recording liquid.

To reduce or eliminate bleeding and improve water resistance, there have been attempts to add emulsion polymers to the recording liquid. For example, disclosed in Japanese Patent Application Laid-Open No. S54-58504 and S54-146109 are recording liquids using oil base dye impregnated with an emulsion polymer, which dye has been obtained by immersing the oil base dye in the emulsion polymer to cause swelling. Japanese Patent Application Laid-Open No. S55-18412 discloses a recording liquid containing an emulsion polymer. Japanese Patent Application Laid-Open No. S62-184072 discloses a recording liquid obtained by reacting an emulsion of a crosslinked polymer with a dye. Japanese Patent Application Laid-Open No. H3-6270 discloses a recording liquid containing an emulsion of a crosslinked polymer. Japanese Patent Application Laid-Open No. H3-160068 discloses a recording liquid containing an emulsion having the minimum film-forming temperature (MFT) of 40° C or higher. Japanese Patent Application Laid-Open No. H3-250069 discloses a recording liquid using an emulsion stained with a dye.

The recording liquids described in the above disclosures do not exhibit sufficient water resistance and light fastness because they are essentially recording liquids using a dye. Moreover, the emulsion polymer tends to cause clogging in the liquid passage of an ink jet printer, particularly at the nozzle. As a consequence, there has been a demand for a binder resin suited for ink jet printing; i.e. resin which permits the stable discharge of recording liquid to a target surface without causing clogging.

55 As a coloring material, pigment possesses excellent water resistance and light fastness. Thus recording liquids containing pigments have been regarded promising. Various types of such liquids have been under investigation. However, since a pigment by itself does not adhere firmly to recording paper or OHP sheet, a binder resin is required in combination. Furthermore, since pigments are insoluble in water, it is difficult to disperse pigment particles stably in an aqueous medium. To overcome these difficulties including those related to the pigment itself, it is necessary to use a binder resin which eliminates clogging of the resulting recording liquid upon discharge and offers improved dispersion stability of the pigment, good water resistance, light fastness, and high resolution of the recorded image.

## SUMMARY OF THE INVENTION

An object of the present invention is to provide an aqueous pigment-type ink jet recording liquid with the requisite characteristics for ink jet printing, in particular, excellent water resistance and light fastness, high resolution of the recorded image and good dispersion stability. Another object of the present invention is to provide an aqueous pigment-type ink jet recording liquid which does not cause clogging in the liquid passage of an ink jet printer, particularly at the nozzle, thereby permitting the stable discharge of the liquid to the printing surface.

The ink jet recording liquid of the present invention produces a recorded image having good water resistance, light fastness and high resolution. Although the ink jet recording liquid of the present invention is aqueous, it has excellent water resistance. Thus it can be used effectively in an office for document preparation, addressing envelopes, marking corrugated cardboards, numbering, printing bar codes and other tasks. The recording liquid of the present invention is superior in light fastness to the prior art dye-type recording liquids. This property enables the production of recorded materials superior in storage stability.

The recording liquid of the present invention can be discharged to the recording surface without causing clogging in the liquid passage of an ink jet printer. Moreover, since it has good dispersion stability, stable operation of the ink jet printer can be maintained for a long period of time.

The ink jet recording liquid of the present invention is an ink jet recording liquid obtained by dispersing pigment and resin in an aqueous medium. The resin employed is an aqueous dispersion-type resin comprising a shell composed of a polymer having a glass transition point of 50° C to 150° C and a core having a glass transition point of -100° C to 40° C.

A process for preparing an ink jet recording liquid of the present invention comprises: a process for preparing an aqueous dispersion-type resin by polymerizing a polymerizable monomer yielding a polymer having a glass transition point of -100° C to 40° C, in an aqueous medium in the presence of a resin-type emulsifying agent composed of a polymer having a glass transition point of 50° C to 150° C; and a process for dispersing said aqueous dispersion-type resin with a pigment in said aqueous medium.

In the ink jet recording liquid of the present invention, the aqueous dispersion-type resin consists of a polymer shell with a high glass transition point and a polymer core with a low glass transition point. This resin is used as a binder which encases pigment particles. The recording liquid, therefore, has good storage stability and can be discharged stably to the recording surface without causing clogging.

Since the strongly hydrophobic core component has a low glass transition point, it can be formed easily into a film. It is assumed that upon the application of the recording liquid onto a recording surface, the core squeezes aside the hydrophilic shell and forms a film containing a uniform mixture of shell and core. Due to the higher glass transition point of the shell, the film thus formed is tough and highly water resistant. This makes it possible to provide printed matter with good water resistance.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

The resin contained in the ink jet recording liquid of the present invention is an aqueous dispersion-type resin consisting of a polymer shell having a glass transition point of 50° C to 150° C and a polymer core having a glass transition point of -100° C to 40° C.

The aqueous dispersion-type resin can most conveniently be obtained by emulsifying and suspending a polymerizable monomer, which, when polymerized, results in a polymer having a glass transition point of -100° C to 40° C, and additives such as a surfactant in an aqueous medium in the presence of a resin-type emulsifying agent composed of a polymer having a glass transition point of 50° C to 150° C; and then adding a water-soluble polymerization initiator to the resulting suspension to cause thermal polymerization.

Various particle shapes and particle sizes of the aqueous dispersion-type resin can be obtained by controlling the polymerization process and the choice of emulsifier. Particles having a particle size of several ten to several thousand nm are usually obtained.

Preferably the average particle size of the aqueous dispersion-type resin is 20-200 nm to prevent the resulting ink jet recording liquid from clogging the nozzle. More preferably, the particle size is in the range of 20-150 nm. The use of coarse particles tend to cause clogging at the printer nozzle. It is thus preferable to limit the fraction of the coarse particles of size larger than 1000 nm to less than 10 wt.% of the aqueous dispersion-type resin.

The resin-type emulsifying agent which forms the shell of the aqueous dispersion-type resin is a polymer having a glass transition point of 50° C to 150° C, preferably 60° C to 120° C. When the polymer has a glass transition point lower than 50° C, the resulting recording liquid produces printed matter of poor water resistance and sometimes creates clogging during discharge of the recording liquid. When the polymer has a glass transition point exceeding 150° C, on the other hand, the dispersibility of the aqueous dispersion-type resin in the aqueous medium deteriorates and leads to undesirable increase in the viscosity of the whole system. Glass transition points outside the above range are therefore not preferred.

The glass transition point (hereinafter abbreviated as "Tg") is determined using an analytical methods such as viscoelasticity measurement or thermal analysis. Alternatively it is calculated by an equation using known values of Tg of the homopolymers of the polymerizable monomer.

The Tg (absolute temperature) of the copolymer when it is composed of two polymerizable monomers (monomer A and monomer B) can be calculated by the equation:

$$100 / (\text{Tg of the copolymer}) = (\text{wt. \% of A} / \text{Tg of the homopolymer of A}) + (\text{wt. \% of B} / \text{Tg of the homopolymer of B}).$$

Tg (absolute temperature) of a copolymer when the copolymer is composed of three polymerizable monomers (monomer A, monomer B and monomer C) is calculated by the equation:

$$100 / (\text{Tg of the copolymer}) = (\text{wt. \% of A} / \text{Tg of the homopolymer of A}) + (\text{wt. \% of B} / \text{Tg of the homopolymer of B}) + (\text{wt. \% of C} / \text{Tg of the homopolymer of C}).$$

Tg of a copolymer composed of four or more monomers can be calculated in a similar manner.

The resin-type emulsifying agent is prepared, for example, as follows: A hydrophilic polymerizable monomer or a mixture of at least two hydrophilic polymerizable monomers is copolymerized with another polymerizable monomer or a mixture of two or more such monomers so that the resulting polymer has a composition corresponding to Tg of 50° C to 150° C. When an anionic-group-containing polymerizable monomer has to be used, it must be followed by neutralization with a base such as an alkali metal hydroxide or amine. When an amino-containing polymerizable monomer is used, on the other hand, it must be followed by neutralization with an acid such as acetic acid or hydrochloric acid. In this manner, one can prepare resin-type emulsifying agent required for this process.

Examples of the polymerizable monomer will be given together with Tg of the homopolymer of the polymerizable monomer in the following:

Examples of the hydrophilic polymerizable monomer include carboxyl-containing polymerizable monomers such as acrylic acid (106° C), methacrylic acid (130° C), itaconic acid (150° C), fumaric acid or maleic acid; sulfonic-acid-containing polymerizable monomers such as 3-sulfopropyl acrylate; amino-containing polymerizable monomers such as N,N-dimethylaminoethyl methacrylate (20° C) or N,N-diethylaminoethyl methacrylate; and amide group polymerizable monomers such as acrylamide (153° C), vinyl acetamide or vinylpyrrolidone.

Examples of another monomer include alkyl acrylates such as methyl acrylate (8° C), ethyl acrylate (-22° C), isopropyl acrylate, butyl acrylate (-53° C), 2-ethylhexyl acrylate (-85° C), lauryl acrylate or stearyl acrylate; alkyl methacrylates such as methyl methacrylate (105° C), ethyl methacrylate (65° C), isopropyl methacrylate, butyl methacrylate (20° C), 2-ethylhexyl methacrylate, lauryl methacrylate (-65° C) or stearyl methacrylate; and reactive polymerizable monomers such as glycidyl acrylate, glycidyl methacrylate (41° C) or acrolein.

Among the polymerizable monomers listed above, carboxyl-containing monomers such as acrylic acid or methacrylic acid are particularly preferred considering the water resistance of the printed matter using the resulting recording liquid and also the cost aspect of the recording liquid. Moreover, it is preferred that the acid value of the resin-type emulsifier using such monomer is 50 mgKOH/g - 250 mgKOH/g, more preferably 100 mgKOH/g to 200 mgKOH/g. When the acid value is lower than the above range, the stability of the aqueous dispersion-type resin is reduced. When the acid value exceeds above range, on the other hand, the water resistance of the printed matter decreases. And further, it is preferred that the number average molecular weight of the resin-type emulsifier using such monomer is 3000-20000, more preferably 5000-15000.

The core of the aqueous dispersion-type resin is formed by a polymer having a glass transition point of -100° C to 40° C, preferably -50° C to 20° C. The glass transition points of the polymer lower than -100° C render the resulting printed matter sticky. It also hinders the stable discharge (which will hereinafter be called "discharge stability") of recording liquid onto the recording surface. When the glass transition point of the polymer exceeds 40° C, on the other hand, a strongly hydrophobic polymer of the core fails to form a film during printing, resulting in poor water resistance of the printed matter.

No particular limitation is imposed on the polymerizable monomer for the synthesis of a polymer which forms the core of the aqueous dispersion-type resin. Preferably, it is a compound having one or more ethylenic unsaturated double bonds. A polymerizable monomer or a mixture of at least two such monomers can be added in such proportion that the resulting polymer has a Tg of -100° C to 40° C. For the synthesis of the core-forming polymer, those used for the resin-type emulsifying agent for the shell such as alkyl (meth)acrylates, carboxyl-containing polymerizable monomers, sulfonic-acid-containing polymerizable monomers and reactive polymerizable monomers can also be employed.

Other examples of the polymerizable monomers for the formation of the core include hydroxyl-containing polymerizable monomers such as hydroxyethyl acrylate (-15° C), hydroxyethyl methacrylate, hydroxypropyl acrylate and

hydroxypropyl methacrylate; and amide base polymerizable monomers such as acrylamide (153° C), methacrylamide, N-methylol acrylamide, N-methylol methacrylamide, di-N-methylol acrylamide, di-N-methylol methacrylamide, vinyl acetamide and vinylpyrrolidone.

Examples also include polyfunctional polymerizable monomers such as ethylene glycol diacrylate, ethylene glycol dimethacrylate, butanediol diacrylate, butanediol dimethacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, polyethylene glycol diacrylate, polyethylene glycol dimethacrylate, trimethylol propane triacrylate, trimethylol propane trimethacrylate, pentaerythritol triacrylate and pentaerythritol trimethacrylate.

In addition, cationic-group-containing polymerizable monomers such as N,N-dimethylaminoethyl acrylate, N,N-dimethylaminoethyl methacrylate (20° C), N,N-diethylaminoethyl acrylate, N,N-diethylaminoethyl methacrylate and vinyl pyridine, styrene (100° C), methylstyrene, vinyltoluene, vinyl acetate, acrylonitrile and butadiene can be given as examples.

It is desirable that the weight ratio of the shell to the core of the aqueous dispersion-type resin falls within a range of 10 : 90 to 70 : 30. When the weight ratio of the shell is smaller than the above range, it becomes impossible to produce a stable aqueous dispersion-type resin. When the weight ratio of the shell exceeds the above range, the resulting printed matter is likely to exhibit poor water resistance.

It is also desirable that the aqueous dispersion-type resin constitutes in a solid form 0.1-10 wt.% of the recording liquid, more preferably 0.5 to 5 wt.%. When the content of the aqueous dispersion-type resin is less than 0.1 wt.%, poor water resistance results. When the content of the aqueous dispersion-type resin exceeds 10 wt.%, on the other hand, the viscosity of the resulting recording liquid increases and stable discharge is hindered.

For pigment, one can use various pigments used for printing ink, paint, etc. The Color Index (C.I.) numbers of such pigments are as follows: C.I. Pigment Yellow 20, 24, 86, 93, 109, 110, 117, 125, 137, 138, 147, 148, 153, 154, 166 and 168; C.I. Pigment Orange 36, 43, 51, 55, 59 and 61; C. I. Pigment Red 9, 97, 122, 123, 149, 168, 177, 180, 192, 215, 216, 217, 220, 223, 224, 226, 227, 228 and 240; C.I. Pigment Violet 19, 23, 29, 30, 37, 40 and 50; C.I. Pigment Blue 15, 15:1, 15:4, 15:6, 22, 60 and 64; C.I. Pigment Green 7 and 36; C.I. Pigment Brown 23, 25 and 26; C.I. Pigment Black 7 and titanium black.

The pigments listed above may be used in the form of an aqueous slurry after the formation of the pigment or may be used in the powdered form obtained by drying the slurry, by spray drying or by allied methods. It is also possible to use surface-treated pigments having a functionalized surface.

The smaller the size of the pigment particles, the better the splash property of the recording liquid. It is thus preferable to use pigment particles having a smaller particle size or to use a pigment which can be finely divided during the dispersion step. The pigment particles have preferably an average particle size not larger than 0.2  $\mu\text{m}$ , preferably not larger than 0.1  $\mu\text{m}$  as measured by centrifugal sedimentation. The use of a pigment of such small particle size facilitates filtering operation during the preparation of the recording liquid and reduces the precipitation as it ages.

For the ink jet recording liquid of the present invention, a dye can be used in combination to adjust the hue or impart the recording density, as long as it is not used in excess resulting in poor water resistance or light resistance. The use of the dye sometimes deteriorates the dispersion stability of the pigment. Accordingly, it is necessary to limit the proportion of the dye to no more than 40 wt.%, preferably no more than 25 wt.% of the pigment.

Examples of the dye usable in the present invention include acid dyes, basic dyes, direct dyes, reactive dyes, disperse dyes and metal-containing dyes. Preferred are purified dyes from which inorganic salts has been removed.

Examples of dyes include C.I. Direct Black 17, 19, 32, 51, 71, 108, 146, 154 and 166; C.I. Acid Black 2, 7, 24, 26, 31, 52, 63, 112 and 118; C.I. Food Black 2; C.I. Basic Black 2; C.I. Direct Blue 6, 22, 25, 71, 90 and 106; C.I. Acid Blue 9, 22, 40, 59, 93, 102, 104, 113, 117, 120, 167, 229 and 234; C.I. Basic Blue 1, 3, 5, 7, 9, 24, 25, 26, 28 and 29; C.I. Direct Red 1, 4, 17, 28 and 83; C.I. Acid Red 1, 6, 32, 37, 51, 52, 80, 85, 87, 92, 94, 115, 180, 256, 315 and 317; C.I. Basic Red 1, 2, 9, 12, 13, 14 and 37; C.I. Direct Yellow 12, 24, 26 and 98; C.I. Acid Yellow 11, 17, 23, 25, 29, 42, 61 and 71; C.I. Basic Yellow 11 and 28; C.I. Direct Orange 34, 39, 44, 46 and 60; C.I. Direct Violet 47 and 48; C.I. Direct Brown 109; C.I. Direct Green 59; C.I. Acid Orange 7 and 19; C.I. Acid Violet 49; C.I. Basic Violet 7, 14 and 27.

The aqueous medium consists of water and an aqueous solvent which has been added as needed.

As water, deionized water from which metal ions have been removed or distilled water can be used in an amount within a range of 49 wt.% to 95 wt.% of the recording liquid.

The aqueous solvent can be used to prevent the drying of the recording liquid at the nozzle, to prevent the solidification of the recording liquid, to permit the stable injection of the recording liquid and to prevent the drying of the nozzle with the passage of time. The aqueous solvent is used in an amount ranging from 1 to 50 wt.%, preferably 2 to 25 wt.% of the recording liquid.

Examples of aqueous solvents include ethylene glycol, diethylene glycol, propylene glycol, 1,3-propanediol, triethylene glycol, polyethylene glycol, glycerin, tetraethylene glycol, dipropylene glycol, ketone alcohol, diethylene glycol monobutyl ether, ethylene glycol monobutyl ether, ethylene glycol monoethyl ether, 1,2-hexane diol, N-methyl-2-pyrrolidone, substituted pyrrolidone, 2,4,6-hexanetriol, tetrafurfuryl alcohol and 4-methoxy-4-methylpentanone.

For aqueous solvent, a combined use of glycerin and 1,3-propanediol is particularly preferred. The use of glycerin as the aqueous solvent makes it possible to impart the recording liquid with sufficient water retention, but glycerin used

alone tends to cause increase in viscosity. Addition of 1,3-propanediol in combination lowers the viscosity of the recording liquid and suppresses viscosity increase of the recording liquid after evaporation of water. Accordingly, when glycerin is used in combination with 1,3-propanediol, the recording liquid is prevented from viscosity increase in the nozzle, and from solidification as it dries and, as a result, clogging of the nozzle is avoided.

It is also possible to use alcohols such as methanol, ethanol or isopropyl alcohol to increase the drying rate of the recording liquid on the recording paper.

Various additives as described below can be added as needed to the ink jet recording liquid of the present invention:

If a recording sheet is water-permeable, as is the case with paper, it is possible to add a penetrant to accelerate the penetration of the recording liquid into paper, thereby improving apparent drying rate.

Examples of the penetrant include glycol ethers such as diethylene glycol and monobutyl ether which have been listed above as the aqueous solvent, and alkylene glycol, polyethylene glycol monolauryl ether, sodium laurylsulfate, sodium dodecylbenzenesulfonate, sodium oleate and sodium dioctylsulfosuccinate. The penetrants are used in an amount ranging from 0 wt.% to 5 wt.%, preferably 1 wt.% to 5 wt.% of the recording liquid. The penetrant brings about desired effect when used in an amount within the above range. When one uses amounts larger than the above range, undesirable bleeding of printed images and print-through result.

A mildewproofing agent serves to prevent the growth of mildew in the recording liquid. Examples of the mildewproofing agent include sodium dehydroacetate, sodium benzoate and sodium pyridinethion-1-oxide, zincpyridinethion-1-oxide, and amine salts of 1,2-benzisothiazolin-3-one or 1-benzisothiazolin-3-one. The mildewproofing agent is used in an amount ranging from 0.05 wt.% to 1.0 wt.% of the recording liquid.

The chelating agent serves to block metal ions in the recording liquid and prevent the precipitation of metals in the nozzle and of insoluble matters in the recording liquid. Examples of the chelating agent include ethylene diamine tetraacetic acid, sodium salt of ethylenediamine tetraacetic acid, diammonium salt of ethylene diamine tetraacetic acid and tetraammonium salt of ethylene diamine tetraacetic acid. The chelating agent is used in an amount ranging from 0.005 wt.% to 0.5 wt.% of the recording liquid.

In addition, a pH regulator such as amine, inorganic salts, and ammonia or a buffer such as phosphoric acid can be added to regulate the pH of the recording liquid, obtain its dispersion stability and protect the tubing of the liquid passage of the ink jet printer.

Moreover, in order to prevent foam generation during circulation and transfer of the recording liquid or during the preparing of the recording liquid, anti-foaming agent can be added.

Furthermore, anionic, nonionic, cationic or amphoteric surfactant can be used to improve pigment dispersion.

Examples of anionic surfactants include fatty acid salts, alkylsulfate ester salts, alkylarylsulfonate salts, alkyl-naphthalenesulfonate salts, dialkylsulfonate salts, dialkylsulfosuccinate salts, alkyl-diaryl ether disulfonate salts, alkylphosphate salts, polyoxyethylene alkylether sulfate salts, polyoxyethylene alkylaryl ether sulfate salts, naphthalenesulfonic acid formalin condensate, polyoxyethylene alkylphosphate ester salts, glycerol borate fatty acid esters and polyoxyethylene glycerol fatty acid esters.

Examples of nonionic surfactant include polyoxyethylene alkyl ethers, polyoxyethylene alkylaryl ethers, polyoxyethylene oxypropylene block copolymers, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene sorbitol fatty acid esters, glycerin fatty acid esters, polyoxyethylene fatty acid esters and polyoxyethylene alkylamines as well as fluorine group and silicon group nonionic surfactants.

Examples of cationic surfactant include alkylamine salts, quaternary ammonium salts, alkyl pyridinium salts and alkyl imidazolium salts.

Examples of amphoteric surfactant include alkylbetaine, alkylamine oxide and phosphatidyl choline.

As another additive, urea, dimethyl urea or the like can also be added.

The ink jet recording liquid of the present invention can be prepared by mixing an aqueous dispersion of a pigment, the aqueous dispersion-type resin described above and, as needed, water and additives, and then dispersing each component in the resulting mixture by a sand mill, homogenizer, ball mill, paint shaker or ultrasonic dispersing machine. Alternatively, the liquid can be prepared by first thoroughly kneading a pigment, a dispersant and an additive in a kneader or a twin-roll mill in advance, dispersing each component in the sand mill or the like, diluting with water as needed, and then mixing the diluted dispersion with the aqueous dispersion-type resin and other additives.

Mixing and stirring can be accomplished by a high-speed dispersion mixer or emulsifier as well as a conventional stirrer equipped with a blade or blades.

It is preferred that the recording liquid is filtered thoroughly prior to or after dilution through a filter having a pore size of 0.65  $\mu\text{m}$  or less, preferably through a filter having a pore size of 0.45  $\mu\text{m}$  or less. Prior to the filtration process through a filter, filtration by centrifugal separator can be added to reduce filter clogging to cut down

the frequency of filter exchange. Viscosity of the prepared recording liquid should be adjusted to fall in the range of 0.8 cps to 15 cps (25° C), depending on the design of the ink jet printer. The surface tension should be 25 to 60 dyne/cm. No particular limitation is imposed on the pH but the pH within a range of 4 to 12 is preferred, and weak alkaline range of 7 to 9 pH is particularly preferred.



## Examples

The present invention will hereinafter be described more specifically based on examples. It should, however, be borne in mind that the scope of the present invention is not limited to or by these specific examples, in which all designations of parts and % indicate parts by weight and weight percentage(wt.%), respectively.

## Emulsion Preparation 1

A 1-liter four-neck flask was equipped with a blade stirrer and a reflux condenser. The flask is charged with 80 parts of methyl methacrylate, 20 parts of acrylic acid, 1 part of azobisisobutyronitrile and 60 parts of isopropanol. The resulting mixture was heated to 80° C while being stirred in flowing nitrogen gas and polymerization reaction was maintained for 10 hours. The resin solution thus obtained was dried under reduced pressure, whereby a resin-type emulsifying agent having a Tg of about 105° C, a number average molecular weight of about 10000 and an acid value of about 110 mgKOH/g was obtained in a solid form. After a 1-liter four-neck flask was equipped with a blade stirrer and a reflux condenser, the flask was charged with 100 parts of the resulting solid resin-type emulsifying agent, 47 parts of 17% aqueous ammonia and 753 parts of purified water. The resulting mixture was stirred and dissolved at room temperature, whereby an aqueous solution of the resin-type emulsifying agent was obtained. To the resulting aqueous solution of the resin-type emulsifying agent, 30 parts of methyl methacrylate, 70 parts of ethyl acrylate, 0.5 part of ammonium persulfate and 0.5 part of Rongalit were added. The resulting mixture was heated to 60°C in a nitrogen gas atmosphere, followed by polymerization reaction at 60° C for 5 hours. What was obtained as a result was an emulsion of an aqueous dispersion-type resin in which the core-forming polymer had a TG of 6°C and an average particle size of the resin was 80 nm. Its ratio of the resin-type emulsifying agent (shell) to the core material was 50 : 50 by weight. The emulsion had a solid resin content of 20%.

## Emulsion Preparations 2-3,

## Emulsion Preparations C1-C3:

Emulsion Preparations 2-3 and Emulsion Preparations C1-C3 (C for comparison) were prepared from the raw materials shown in Table 1 for the shell and core. These emulsions of an aqueous dispersion-type resins were obtained by the same procedures used for Emulsion Preparation 1.

Incidentally, in Table 1, "MMA", "AA", "EA", "St", "MAA", "EHA", "BMA" and "BA" represent methyl methacrylate, acrylic acid, ethyl acrylate, styrene, methacrylic acid, 2-ethylhexyl acrylate, butyl methacrylate and butyl acrylate, respectively.

## Emulsion Preparation C4

The emulsion of an aqueous dispersion-type resin was prepared by using a surfactant as follows:

A 1-liter four-neck flask was equipped with a blade stirrer and a reflux condenser. The flask was charged with 5 parts of an anionic surfactant ("EMAL O" produced by Kao Corporation), 3 parts of a nonionic surfactant ("EMULGEN 950" produced by Kao Corporation), 491 parts of purified water, 30 parts of methyl methacrylate, 70 parts of ethyl acrylate, 0.5 part of ammonium persulfate and 0.5 part of Rongalit. The resulting mixture was heated to 60° C in flowing nitrogen gas and polymerization reaction was maintained at 60°C for 5 hours. As a result, an emulsion of an aqueous dispersion-type resin with a TG of 6° C and an average particle size of 100 nm was obtained. Its solid resin content was 20%.

## Example 1

20 parts of C.I. Pigment Black 7 ("MONARCH 800"; carbon black produced by CABOT Corporation), 5 parts of an anionic surfactant ("EMAL 10" produced by Kao Corporation), 5 parts of a nonionic surfactant ("EMULGEN 920" produced by Kao Corporation) and 70 parts of purified water were mixed. This mixture was then subjected to dispersion in a sand mill for 2 hours after which a water dispersion of black pigment particles with an average particle size of about 100 nm was obtained. 20 parts of the resulting water dispersion of the black pigment (pigment content: 4%), 15 parts of the emulsion of an aqueous dispersion-type resin (solid content: 20%) of Emulsion Preparation 1, 10 parts of glycerin, 0.1 part of a mildewproofing agent ("Sodium Omadine" produced by OLIN CHEMICALS) and 54.9 parts of purified water were stirred and mixed in a disper. The resulting mixture was then filtered through a membrane filter made of nitrocellulose with a pore size of 0.45 µm. The filtrate thus obtained was the black ink jet recording liquid.

## Examples 2-4, Examples C1-C4

In these instances, each ink jet recording liquid was obtained by the same procedure as in Example 1 using the emulsion of the aqueous dispersion-type resins (solid content: 20%) prepared as Preparations 1-3 or Preparations C1-C4. Components used for the preparation of those ink jet recording liquids are shown in Table 2.

## Example C5

C5 was prepared to show comparison between the ink jet recording liquid prepared using the pigment of the present invention and a prior art ink jet recording liquid prepared using a dye. Ink jet recording liquid C5 was thus prepared using Food Black 2 as a dye instead of a pigment and the emulsion of the aqueous dispersion-type resin (solid content: 20%) of Emulsion Preparation 1.

Particle size and viscosity measurements were made and storage stability, discharge stability, water resistance and clogging resistance were evaluated on each of the ink jet recording liquids 1-4 and C1-C5. Results are shown in Table 2. The measurements and evaluations were conducted as described in the following:

## (1) Particle size

The particle size distribution of the recording liquid was measured by a particle-size-distribution gauge using a laser diffraction method ("DSL-700", manufactured by Ohtsuka Denshi Co., Ltd.). Average particle size was then calculated.

## (2) Viscosity

The viscosity at 25° C was measured by a vibration viscometer ("VM-1A" manufactured by Yamaichi Denkisha Co, Ltd.).

## (3) Storage stability

The recording liquid was stored at 50° C for three months. Storage stability was evaluated based on the change in the particle size after aging. In Table 2, "○" indicates that the change in the particle size was less than 15 nm, while "X" indicates that the change in the particle size was 15 nm or greater.

## (4) Discharge stability

The recording liquid was loaded in the cartridge of an ink jet printer ("HG-5130", manufactured by Seiko Epson Co., Ltd.). Discharge stability was evaluated by printing on paper ("K", produced by Xerox Corporation). In Table 2, "○" indicates that the recording liquid was discharged stably from the nozzle, while "X" indicates that the recording liquid was not discharged stably from the nozzle.

## (5) Water resistance

The printed matter obtained in (4) was moistened with water and then the printed surface was rubbed by a finger. Changes, if any, in the printed portion was visually inspected. In Table 2, "○" indicates that neither bleeding nor peeling of the ink was detected, and "X" indicates that bleeding or peeling of the ink was observed.

## (6) Clogging resistance

After the printing in (4), the cap was removed from the printer head. Printing was resumed one hour later and presence or absence of clogging was noted. In Table 2, "○" indicates that the nozzle was not clogged, and "X" indicates that the nozzle was clogged.

In Table 2, surfactant A, surfactant B, surfactant C and surfactant D represent an anionic surfactant ("EMAL 10" produced by Kao Corporation), a nonionic surfactant ("EMULGEN 920" produced by Kao Corporation), an anionic surfactant ("Newcol 565SNC" produced by Nippon Nyukazai Co., Ltd.) and a nonionic surfactant ("Solsperse 27000", produced by Degussa AG), respectively.

Table 1

		Emulsion Preparation			Emulsion Preparation C		
		1	2	3	C1	C2	C3
Resin-type emulsifying agent	Composition (part)	MMA (80) AA (20)	St (70) MAA (30)	BMA (50) MAA (50)	BMA (80) AA (20)	MMA (80) AA (20)	BMA (80) AA (20)
	Number average molecular weight	10,000	6,000	10,000	10,000	10,000	10,000
	Tg	105°C	109°C	66°C	34°C	105°C	34°C
	Acid value (mgKOH/g)	110	140	230	110	110	110
Core	Composition (part)	MMA (30) EA (70)	St (70) EHA (30)	BA (100)	MMA (30) EA (70)	St (80) EA (20)	St (80) EA (20)
	Tg	6°C	15°C	-53°C	6°C	67°C	67°C
Weight ratio of shell to core		50/50	30/70	50/50	50/50	40/60	50/50
Average particle size of resin		80 nm	90 nm	80 nm	80 nm	80 nm	90 nm

Table 2:

	Examples					C				
	1	2	3	4		C1	C2	C3	C4	C5
Dispersion of pigment	Pigment (C.I.) (part)	Black 7 (20)	Red 122 (20)	Yellow 74 (20)	Red 122 (20)	Black 7 (20)	Black 7 (20)	Red 122 (20)	Black 7 (20)	/
	Surfactant (part)	A (5) B (5)	C (5) D (3)	A (5) B (3)	C (5) D (3)	A (5) B (5)	A (5) B (5)	C (5) D (3)	A (5) B (5)	/
	Purified water	70 parts	72 parts	72 parts	72 parts	70 parts	70 parts	72 parts	70 parts	/
	Average particle size	80 nm	100 nm	80 nm	100 nm	80 nm	80 nm	100 nm	80 nm	/
	Pigment dispersion	20 parts	10 parts	20 parts	10 parts	20 parts	20 parts	10 parts	20 parts	/
Recording liquid	Dye (part)	/	/	/	/	/	/	/	/	Food black 2 (3.5)
	Emulsion of a resin (part)	Prep. 1 (15)	Prep. 2 (15)	Prep. 3 (20)	Prep. 2 (15)	Prep. C1 (15)	Prep. C2 (15)	Prep. C3 (15)	Prep. C4 (15)	Prep. 1 (15)
	Glycerin	10 parts	10 parts	10 parts	5 parts	10 parts	10 parts	10 parts	10 parts	10 parts
	1,3-propanediol	/	/	/	10 parts	/	/	/	/	/
	Mildewproofing agent	0.1 parts	0.1 parts	0.1 parts	0.1 parts	0.1 parts	0.1 parts	0.1 parts	0.1 parts	0.1 parts
Evaluation results	Purified water	54.9 parts	64.9 parts	49.9 parts	59.9 parts	54.9 parts	54.9 parts	64.9 parts	54.9 parts	71.4 parts
	Average particle size	90 nm	90 nm	90 nm	90 nm	90 nm	90 nm	90 nm	100 nm	80 nm
	Viscosity	1.7 cps	1.5 cps	1.8 cps	1.7 cps	1.7 cps	1.7 cps	1.5 cps	1.5 cps	1.3 cps
	Storage stability	○	○	○	○	○	○	○	×	○
	Discharge stability	○	○	○	○	○	○	○	×	○
	Water resistance	○	○	○	○	×	×	×	○	×
	Clogging resistance	○	○	○	○	○	○	○	×	○

Prep.: Emulsion Preparation, Prep.C : Emulsion Preparation, Series C.

## Claims

1. An ink jet recording liquid obtained by dispersing a pigment and a resin in an aqueous medium, said resin being an aqueous dispersion-type resin comprising a shell composed of a polymer having a glass transition point in the range of 50° C to 150° C and a core composed of a polymer having a glass transition point in the range of -100° C to 40° C.
2. An ink jet recording liquid of claim 1, wherein the polymer forming the shell has a glass transition point in the range of 60° C to 120° C and the polymer forming the core has a glass transition point in the range of -50° C to 20° C.
3. An ink jet recording liquid of claim 1, wherein the aqueous dispersion-type resin has an average particle size in the range of 20 nm to 200 nm.
4. An ink jet recording liquid of claim 1, wherein the aqueous dispersion-type resin contains resin particles having a particle size of at least 1000 nm in an amount equal to or less than 10 wt.% of the aqueous dispersion-type resin.
5. An ink jet recording liquid of claim 1, wherein the aqueous dispersion-type resin is contained in an amount in the range of 0.1 to 10 wt.% of the recording liquid.
6. An ink jet recording liquid of claim 5, wherein the aqueous dispersion-type resin is contained in an amount in the range of 0.5 to 5 wt.% of the recording liquid.
7. An ink jet recording liquid of claim 1, wherein the weight ratio of the shell to the core falls within the range of 10 : 90 to 70 : 30.
8. An ink jet recording liquid of claim 1, wherein the polymer forming the shell contains a carboxyl group and has an acid value of 50 to 250 mgKOH/g.
9. An ink jet recording liquid of claim 1, wherein the aqueous medium contains glycerin and 1,3-propane diol.
10. A process for the preparation of an ink jet recording liquid, which comprises a step of preparing an aqueous dispersion-type resin by polymerizing a polymerizable monomer, which provides a polymer having a glass transition point of -100° C to 40° C, in an aqueous medium in the presence of a resin-type emulsifying agent composed of a polymer having a glass transition point in the range of 50° C to 150° C, and a step of dispersing the resulting aqueous dispersion-type resin with a pigment in the aqueous medium.



(19)



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**(54) Ink jet recording liquid**

(57) The present invention relates to an aqueous ink jet recording liquid of a pigment type, which liquid has excellent stability and printing characteristics; and also to a process for the preparation of said liquid. The ink jet recording liquid of the present invention is obtained by dispersing a pigment and a resin in an aqueous medium. Said resin is an aqueous dispersion-type resin comprising a shell composed of a polymer having a glass transition point in the range of 50° C to 150° C and a core composed of a polymer having a glass transition point in the range of -100° C to 40° C.

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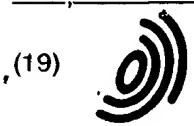
# EUROPEAN SEARCH REPORT

Application Number  
EP 97 10 4413

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 392 (C-0873), 4 October 1991 & JP 03 160069 A (SEIKO EPSON CORP), 10 July 1991, * abstract *	1	C09D11/00
A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 248 (C-0843), 25 June 1991 & JP 03 079679 A (KAO CORP), 4 April 1991, * abstract *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C09D
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		15 May 1998	Girard, Y
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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### (54) **Two component dispersant for wet milling process**

(57) A process for preparing an aqueous dispersion by wet milling an aqueous carrier medium, a particulate solid, and a polymeric dispersant; wherein the polymeric dispersant is a combination of at least 50% by weight of a block copolymer; and a random copolymer; and wherein the block and random copolymers are prepared from substantially the same monomers. This invention provides an easy dispersion process for particulate solids, in particular colorants such as pigments or disperse dyes, at higher loadings, and a reduction of dispersion time which improves the productivity. Resulting dispersions have particular utility as inks for ink-jet printers.

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## Description

### FIELD OF THE INVENTION

5 This invention relates to an improved wet milling dispersion process using a unique combination of a block copolymer and a random copolymer of similar composition as the dispersant. The process provides higher loading of particulate solids, with smaller particle size and shorter processing times. The dispersions are particularly suited for preparing pigmented inks for ink-jet printers.

### 10 BACKGROUND OF THE INVENTION

Water-based pigment dispersions are well known in the art, and have been used commercially for applying films, such as paints, to various substrates. The pigment dispersions generally are prepared by a dry method, such as 2-roll or 3-roll milling, or a wet method, such as media milling. The dry milling method includes a milling step wherein the dispersant and the pigment are intimately mixed and milled utilizing mechanical forces to cause particle size reduction and adsorption of the polymer to the pigment surface; a grinding step wherein the pigment dispersion is reduced to small chips; and an inversion step where the chips are dissolved in an aqueous carrier medium. In the wet milling method, particle size reduction and dispersion stabilization are conducted in one step in the presence of the aqueous carrier medium.

20 The dispersant used in a wet milling process must effectively wet the pigment surface and achieve a stable pigment dispersion. Random copolymer dispersants have been disclosed for this purpose, wherein the resulting aqueous dispersion is used as an ink-jet printer ink, in U.S. Patent 4,597,794 (Ohta et al.) assigned to Canon. Block copolymer dispersants, having a hydrophobic block that links to the pigment particles and a hydrophilic block, also are disclosed for this purpose in U.S. Patent 5,085,698 (Ma et al.) assigned to DuPont.

25 Block copolymer dispersants offer improved dispersion stability (compared to random polymer dispersants) because they provide both a charge double layer and steric stabilization. The block copolymers are difficult to manufacture, however, and tend to form stable micelles in the dispersion due to their structure. These micelles, with the hydrophobic pigment-binding segments buried in the core, do not wet the pigment surface as effectively as may be desired. Also, the block copolymers tend to have a high viscosity, which hinders the milling process and requires a reduction in pigment loading for successful milling to occur.

30 Surfactants may be added to facilitate pigment wetting and to reduce dispersion viscosity, thereby addressing the problems discussed above. The addition of surfactants, however, tends to change other physical properties of the dispersion (such as surface tension), and may render the dispersion unsuitable for a desired application. For example, the surfactant may adversely affect dispersion stability; and/or, when the resulting dispersion is used as an ink, the ink tends to have a low surface tension that causes image feathering and general poor print quality.

35 Accordingly, a need continues for an improved dispersion process for preparing aqueous dispersions in general, and in particular for preparing aqueous pigmented inks that are particularly suited for use in ink-jet printers and contain high-loading levels of small pigment particles.

### 40 SUMMARY OF THE INVENTION

It now has been found that the presence of certain random polymers in aqueous particulate dispersions having a block copolymer dispersant enhance wetting of the particles, and enable the particulate loading to be increased without adversely affecting physical properties such as surface tension. Accordingly, in one aspect the invention provides a dispersion having an aqueous carrier medium, at least one particulate solid, and a polymeric dispersant that is a mixture of a block copolymer and a random copolymer, wherein (i) the block and random copolymers are prepared from substantially the same monomers; and (ii) the random copolymer is present in the amount of 1 to 100 parts by weight per 100 parts, by weight, of the block copolymer.

45 In another aspect, the invention provides a process for preparing an aqueous dispersion by wet milling an aqueous carrier medium, at least one particulate solid, and a polymeric dispersant that is a mixture of a block copolymer and a random copolymer, wherein (i) the block and random copolymers are prepared from substantially the same monomers; and (ii) the random copolymer is present in the amount of 1 to 100 parts by weight per 100 parts, by weight, of the block copolymer. The process achieves high loadings of the particulate solid (e.g., a pigment or disperse dye) during a short time, which improves productivity.

### 50 DETAILED DESCRIPTION OF THE INVENTION

The invention provides a unique mixture of a block copolymer to provide the dispersion stability, and a random

copolymer of substantially the same composition to enhance the wetting of the surface of the particulate solid. This unique mixture of dispersants allows a higher loading of particulate solid for higher productivity, without adversely affecting the physical properties of the dispersion such as surface tension. For example, the resulting dispersion may contain up to 50% or 60% dispersed solids, based on total weight of the dispersion. This loading of particulate solids is up to twice the amount that can be achieved when the block dispersants are used alone. Resulting pigment dispersions are particularly suited for use with ink jet printers in general, and thermal ink jet printers in particular.

#### AQUEOUS CARRIER MEDIUM

The aqueous carrier medium is water or a mixture of water or at least one water soluble organic component. Deionized water is commonly used. The organic component may be an organic solvent, polymeric binder, thickener, thixotropic agent, coating aid, etc.

For ink jet inks, the aqueous carrier medium is typically a mixture of water and at least one water-soluble organic solvent. Representative examples of water-soluble organic solvents are disclosed in U.S. Patent 5,085,698. Selection of a suitable mixture of water and water soluble organic solvent depends upon requirements of the specific application, such as desired surface tension and viscosity, the selected pigment, desired drying time, and the type of media substrate onto which the coating or ink will be printed. A mixture of diethylene glycol and deionized water is preferred as the aqueous carrier medium for ink jet inks, with the composition typically containing between 30% and 95% (preferably 60% to 95%) water by weight, based on the total weight of the mixture.

The amount of aqueous carrier medium in the ink is in the range of approximately 70 to 99.8%, preferably at least 94%, based on the total weight of the ink when the particulate solid is an organic pigment, and approximately 25 to 99.8% when the particulate solid is an inorganic pigment.

#### PARTICULATE SOLIDS

The particulate solid may be an insoluble colorant (such as a pigment or disperse dye), colloidal silver halide, metallic flake, a herbicide, an insecticide, or biomaterials (such as drugs) depending upon the particular application of the dispersion. For example, if the intended use is in an ink or a paint, the particulate solid is an aqueous carrier medium insoluble colorant such as a pigment, disperse dye, or a mixture thereof.

The particulate solid selected must be capable of binding with the hydrophobic portion of the block copolymer. Preferably, the particulate solids have "binding sites" that permit binding with the polymer. Most of the above-mentioned particulate solids have very specific functional groups on their surfaces.

For example, all carbon blacks have chemisorbed oxygen complexes, primarily acidic in nature (e.g. carboxylic, quinonic, lactonic or phenolic groups) on their surfaces to varying degrees, depending on the conditions of manufacture. These acidic groups provide binding sites for dispersants having basic functional groups, such as amine groups. Other pigments have basic surfaces. The pigment itself may contain functional groups, or the surfaces may be modified by compounds containing functional groups such as sulfonic acid, phosphoric acid, and carboxylic acid groups or amine-type of basic groups. All are equally useful for this invention. Furthermore, almost all of the organic color pigments and many of the surface treatment compounds have aromatic features in their structures, providing sites for additional aromatic interactions with the dispersant. Examples of pigments that may be used to form the composition include azo, anthraquinone, thioindigo, oxazine, quinacridone, lakes and toners of acidic or basic dye stuffs, copper phthalocyanine and its derivatives, and various mixtures and modifications thereof.

The particle size has an influence on the dispersion stability. Brownian motion of minute particles helps prevent flocculation and settling. The particle size thus should be selected to optimize the stability of the dispersion, consistent with the other requirements of the intended application for the dispersion.

For example, in ink jet ink applications, the pigment particles need to be sufficiently small to permit free flow of the ink through the ink jet printing device, especially at the ejecting nozzles that usually have a diameter in the range of 10 to 50 microns. In addition, it also is desirable to use small particles for maximum color strength and gloss. The useful range of particle size is approximately 0.005 micron to 15 micron. Preferably, the pigment particle size should range from 0.005 to 1 micron.

Also in the case of pigments, the selected pigment may be used in dry or wet form. For example, pigments are usually manufactured in aqueous media and the resulting pigment is obtained as water-wet presscake. In presscake form, the pigment is not aggregated to the extent that it is in dry form. Thus, pigments in water-wet presscake form do not require as much deaggregation in the process of preparing the inks as dry pigments. Representative commercial dry and presscake pigments that may be selected to advantage are disclosed in the aforementioned U.S. Patent 5,085,698.

Fine particles of metal or metal oxides (such as copper, iron, steel, aluminum, silica, alumina, titania, and the like) may be used in the preparation of magnetic ink jet inks and other coating applications for the electronic industries.

DISPERSANTS

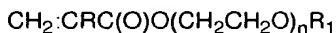
A mixture of at least one block copolymer and at least one random copolymer is used as the dispersant to effectively wet the surface of the particulate solid and to stabilize the dispersion.

Block Copolymer:

The block copolymers suitable for practicing the invention include AB, BAB, and ABC structures. They may be anionic, cationic or non-ionic. These block copolymers must contain hydrophobic and hydrophilic blocks and balanced block sizes to contribute to the dispersion stability. Functional groups can be built into the hydrophobic (pigment binding) block for stronger specific interactions between the pigment and the polymer dispersant to provide improved dispersion stability. Preferred AB and BAB block copolymers, and their process of preparation, are disclosed in U.S. Patents 5,085,698 and 5,272,201. ABC block copolymers, and their methods of preparation, are disclosed in US Patent 5,219,945 and European Patent Application 0 556 649 A1 published August 28, 1993.

In ABC block copolymers, the B block is a hydrophobic homopolymer or random copolymer that serves to bind with the pigment. The A block is a hydrophilic homopolymer or random copolymer or salt thereof, which is solvated by the aqueous carrier medium and serves to stabilize the dispersion by steric and/or double charge layer mechanisms. The C block is commonly an alkylated poly(oxyethylene) substituted (meth)acrylate that is compatible with common organic water-miscible solvents. The C block provides additional dispersion stability.

The preferred structure of the C block monomer is:



wherein R = -H or -CH<sub>3</sub>; R<sub>1</sub> = C<sub>a</sub>H<sub>2a+1</sub> where a = 0-4; and n = 1-20. Examples of these monomers are ethoxyethyl methacrylate, butoxyethyl methacrylate, and ethoxypolyethyleneglycol methacrylate (polyoxyethylene of MW = 44 - 1000).

The block copolymer is present in at least 50% by weight, preferably 50 to 98% by weight, and more preferably 75 to 98% by weight, based on the total weight of the polymeric dispersant combination of block copolymer and random copolymer.

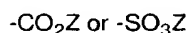
Random Copolymer:

The random copolymer is prepared using substantially the same monomers as those used in preparation of the block copolymers, and should have substantially the same or similar composition as the block copolymer. This means either exactly the same set of monomers or structurally related monomer sets should be used, and about the same percentage per each type of monomers. The ionic character, (anionic, cationic or nonionic) accordingly will be compatible with that of the block copolymer to avoid flocculation. Furthermore, it is preferred that the molecular weight of the random copolymer be close to that of the block copolymer.

The random copolymers may be prepared by any of a number of polymerization methods well known in the art. It is preferred that monomers containing the free acids or free amines of the ionic moieties be polymerized, and the moieties then converted to their salt form after the polymer structure is formed. Exemplary polymerisation methods include free radical solution, emulsion, suspension, bulk polymerization and the like (using a chain transfer agent, if necessary). Other polymerization methods include anionic and group transfer polymerization as described in U.S. Patent No. 4,508,880. Polymers so prepared have precisely controlled molecular weight and very narrow molecular weight distribution.

The random copolymer is present in the range of approximately 0.5 to 50% by weight, preferably 2 to 25%, based on the total weight of the polymeric dispersant combination of block copolymer and random copolymer.

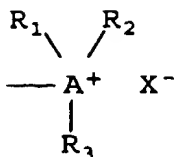
Suitable anionic polymers have a backbone prepared from ethylenically unsaturated units and at least one, and preferably more than three, pendant ionic moieties derived from an anionic unit on the monomer and having the general formula:



wherein Z is selected from conjugate acids of organic bases, alkali metal ions, ammonium ion, and tetraalkylammonium ions. The number of pendant ionic moieties should be sufficient to make the anionic polymers soluble in the aqueous carrier medium and will vary depending on the molecular weight. For the block copolymers, these pendant ionic moieties are mostly concentrated in the hydrophilic block.

Suitable cationic polymers have a backbone prepared from ethylenically unsaturated units and at least one, and preferably more than three, pendant ionic moieties derived from a cationic unit on the monomer and having of the gen-

eral formula:



wherein A is N, P, or S; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> independently are H, alkyl of 1 to 20 carbon atoms, alkyl ether of 1 to 20 carbon atoms, or aryl of 1 to 9 carbon atoms, or alkylaryl of 1 to 9 carbon atoms, with the proviso that R<sub>3</sub> is not present when A is S; and wherein X is an anion selected from the group consisting of halides, conjugate bases of organic acids, and conjugate bases of inorganic acids. The cationic polymers containing phosphonium and sulfonium moieties preferably are made by reacting a halogenated copolymer (e.g., polymer containing 2-bromoethyl methacrylate) with tri-substituted phosphines (e.g., triphenylphosphine) or di-substituted sulfides (e.g., dimethylsulfide). The number of pendant ionic moieties should be sufficient to make the cationic polymer soluble in the aqueous carrier medium and will vary depending on the molecular weight of the polymer. For the block copolymers, these pendant ionic moieties are mostly concentrated in the hydrophilic block.

Strong interaction of a pigment with a dispersant polymer is obtained when the dispersant has one or more attached structures which are the same as the pigment. A common way that this may be accomplished is through general hydrophobic attraction between the polymer and the pigment surface. The pigment often is pretreated with substances that render the surface hydrophobic. A polymer with hydrophobic sites can bind to such a surface through hydrophobic interactions.

A second way in which a dispersant polymer can bind to a solid particulate is through aromatic interactions. If the solid particulate contains aromatic or aromatic-like groups, or if its surface has been pretreated with an aromatic substance, then the aromatic groups in the hydrophobic site can further improve the binding force to the solid particulate.

A third way in which a dispersant polymer can bind to a solid particulate is through ionic bonds. For example, a solid particulate containing sulfonic acid groups can bind strongly to a polymer having basic groups, such as amine groups.

Similarly, a pigment containing quaternary ammonium groups can bind to a polymer through acid groups.

Covalent bonding provides a fourth, and especially strong, mode of binding a dispersant polymer to a solid particulate. For example, a solid particulate with carboxylic groups will react with a polymer containing epoxy groups to form ester linkages. Thus, a polymer containing glycidyl methacrylate groups in the hydrophobic site will form strong links to a carboxylic acid-containing solid particulate.

The amount of the dispersant selected depends on the structure, molecular weight, and other properties of the polymers, and upon the pigment type and other components in the pigment dispersion. The dispersant polymers (i.e., both the block and random copolymer components) have a number average molecular weight below 20,000, preferably below 10,000, and typically in the range of 1,500 to 6,000. The polymeric dispersant mixture of block and random copolymers is present in the range of approximately 0.1 to 30% by weight, preferably 0.1 to 15%, based on the total weight of the pigment dispersion composition. If the amount of the dispersant polymers becomes too large, the viscosity will increase and hinder the dispersion process. If too little is present, the dispersion stability is adversely affected. The ratio of block copolymer to random copolymer is in the range of 100 to 1 by weight block copolymer per part random copolymer, preferably 50 to 2.5 parts block copolymer per part random copolymer, based on the weight. The optimal ratio depends on the specific block copolymer and random copolymer that is selected.

#### DISPERSION PROCESS

The dispersion process is a wet milling process. Wet milling means the entire process of deflocculation, size reduction of the particulate solid, and stabilization of the dispersion is carried out in the presence of an aqueous carrier medium. Usually, the selected block and random copolymers are first neutralized/dissolved in the aqueous carrier medium to prepare a polymer solution at about 10 to 25% solids. The block and random copolymer solutions may be prepared separately and combined before use, or a solution of both polymers can be prepared directly. The selected particulate solid is added to the polymer solution, preferably with agitation to prepare a premix.

The deflocculating (i.e., dispersing) step may be accomplished using a conventional media mill with a wide range of media including pebbles, stainless steel beads, glass beads, zirconium beads, plastic particles such as polycarbonate, etc. The type and size of the media selected is determined by the properties of the particulate solid (e.g. the hardness, ease of fracturing the agglomerates), and the desired particle size for the intended use. The conventional mills (including the horizontal mill, ball mill, or attritor) operate mechanically by agitating the media to produce collision

and shearing forces among the media. The particulate solid is ground by the media, with new surfaces being generated as the size of the particles are reduced. The dispersant polymers are adsorbed onto these newly generated surfaces, preventing the particles from flocculating together, and thereby stabilizing the dispersion. Alternatively, this step may be accomplished without using media by passing the premix through a plurality of nozzles within a liquid jet interaction chamber, under a liquid pressure of at least 1000 psi, to produce the required collision and shearing forces among the particles to achieve particle size reduction and adherence of the polymeric dispersant onto the newly generated surfaces. Commercial units of this type are available from Microfluidics Corp., Watham, MA.

Loading of the particulate solid may be as high as 60%, but will generally be in the range of approximately 10 to 50% by weight, based on the total weight of the dispersion. The loading for an inorganic pigment, having a specific gravity higher than the typical organic pigments, may be as high as 75% by weight based on the total weight of the dispersion. Optimal loading of the selected particulate solid for the desired application, and the optimal ratio of the particulate solid to the polymer, is determined by the viscosity of the dispersion and is determined by routine experimentation.

#### ADDITIVES

Depending on the the specific application, various types of additives can be used to modify the properties of these dispersions. Examples include organic cosolvents, coalescing agents, polymeric binders, thickeners, thixotropic agents, surfactants, coating aids, biocides, sequestering agents, and the like.

For ink jet ink applications, anionic, cationic, nonionic, or amphoteric surfactants maybe present in the amount of 0.01 to 5%, and preferably 0.2 to 2%, based on the total weight of the ink. Biocides such as Dowicides® (Dow Chemical, Midland, MI), Nuosept® (Huls America, Inc., Piscataway, NJ), Omidines® (Olin Corp., Cheshire, CT), Nopcocides® (Henkel Corp., Ambler, PA), Troysans® (Troy Chemical Corp., Newark, NJ), and sodium benzoate; sequestering agents such as EDTA; and other known additives, such as humectants, viscosity modifiers and other polymers may also be added to improve various properties of the ink compositions.

In a preferred embodiment, the dispersion is employed as an ink for ink jet ink printers. The preferred formulation for this application is:

(a) aqueous carrier medium: approximately 70% to 96%, preferably 80% to 96%, based on total weight of the ink when an organic pigment is selected; approximately 25% to 96%, preferably 70% to 96%, when an inorganic pigment is selected;

(b) pigments: up to approximately 30% pigment by weight for organic pigments, but generally in the range of approximately 0.1 to 15%, preferably 0.1 to 8%, by weight of the total ink Composition; with inorganic pigments (which have higher specific gravities), higher concentrations are employed, and may be as high as 75% in some cases;

(c) dispersant polymer combination: approximately 0.1 to 30% preferably 0.1 to 8%, by weight of the total ink composition.

Many ink performance features such as the drop velocity, separation length of the droplets, drop size, and stream stability are greatly affected by the surface tension and the viscosity of the ink. Pigmented ink jet inks suitable for use with ink jet printing systems typically have a surface tension in the range of about 20 to 70 dyne/cm, preferably 30 to 70 dyne/cm, at 20°C. Acceptable viscosities are no greater than 20 cP, and preferably in the range of about 1.0 cP to about 10 cP, at 20°C.

The invention will now be further illustrated, but not limited, by the following examples.

#### EXAMPLES

The random and block copolymers were prepared using the following procedures:

A double slash in the copolymer name indicates a separation between the blocks and a single slash indicates a random copolymer. The values recited in parenthesis represent the degree of polymerization for each monomer.

Preparation I: Random copolymer, poly(ethoxytriethyleneglycol methacrylate-co-benzyl methacrylate-co-methacrylic acid), ETEGMA/BzMA/MAA, (4/15/12)

To a solution of 58.6 g (0.253 mol) of 1,1-bis(trimethylsiloxy)-2-methyl-propene and 2.5 g of tetrabutyl ammonium m-chlorobenzoate (1.0M solution in acetonitrile) in 1120 g tetrahydrofuran (dried by passing it through a column of alumina) was slowly added a mixture of 478.8 g (3.03 mol) trimethylsilyl methacrylate, 666.4 g (3.78 mol) of benzyl methacrylate (dried over molecular sieves), and 251.4 g (1.02 mol) of ethoxytriethyleneglycol methacrylate (dried over molecular sieves), in 50 minutes, under nitrogen atmosphere. The temperature rose from 25.4 °C to 73.5 °C during the

course of the addition. The mixture was stirred overnight. It was quenched with 250 g of methanol. The mixture was distilled until 1410 g of volatiles were collected and 1440 g of 2-pyrrolidone were added to yield 2857 g of a 42% polymer solution.

The random polymer was neutralized using the following procedure: 476.2 g of the polymer were mixed with 59.6 g of potassium hydroxide solution (46.4% in deionized water) and 1464.2 g of deionized water until a homogeneous 10% polymer solution was obtained.

**Preparation II:** Block copolymer, poly(methacrylic acid-b-benzyl methacrylate-b-ethoxytriethylene glycol methacrylate), MAA/BzMA/ETEGMA (12//15//4)

To a solution of 146.5 g (0.63 mol) of 1,1-bis(trimethylsiloxy)-2-methyl-1-propene and 3.5 g of tetrabutyl ammonium m-chlorobenzoate (1.0 M solution in acetonitrile) in 3000 g THF was slowly added, 1197.3 g (7.58 mol) of trimethylsilyl methacrylate, in 25 minutes, under nitrogen atmosphere. The temperature rose from 22.3 °C to 51.1 °C during the course of the addition. When the temperature fell to 41.0 °C, 70 minutes later, 0.5 mL of tetrabutyl ammonium m-chlorobenzoate was added and no exotherm was detected. To the reaction mixture was then slowly added 1666.1 g (9.46 mol) of benzyl methacrylate (dried over molecular sieves) in 45 minutes. The temperature rose to 61.8 °C during the course of the addition. When the temperature fell to 28.3 °C, about 100 minutes later, 0.5 mL of tetrabutyl ammonium m-chlorobenzoate was added and no exotherm was detected. To the reaction mixture was then added 628.6 g (2.56 mol) of ethoxytriethyleneglycol methacrylate (dried over molecular sieves) over 20 minutes. The temperature rose to 31.8 °C. The reaction mixture was stirred for 2.5 hours. It was quenched with 525 g of methanol and stirred overnight. The mixture was distilled until 2600 g of volatiles were collected, and 1700 g of 2-pyrrolidone were added. Further distillation removed 924.2 g of volatiles, and another 2351.9 g of 2-pyrrolidone were added to yield a 39% polymer solution.

The block polymer was neutralized using the following procedure: 131 g of the polymer were mixed with 17.6 g of potassium hydroxide solution (46.4% in deionized water) and 482.8 g of deionized water until a homogeneous 10% polymer solution was obtained.

**Preparation III:** Block copolymer, poly(methacrylic acid-b-benzyl methacrylate-b-ethoxytriethylene glycol methacrylate), MAA/BzMA/ETEGMA (12//18//4)

The polymer was prepared using a procedure similar to that described in Preparation II. A polymer solution of MAA/BzMA/ETEGMA (12//18//4) composition at 39.6% solid in 2-pyrrolidone was obtained.

The block polymer was neutralized using the following procedure: 350 g of the polymer were mixed with 38.3 g of potassium hydroxide solution (45.6% in deionized water) and 536.5 g of deionized water until a homogeneous 15% polymer solution was obtained.

#### Control 1:

A pigment dispersion was prepared using the polymer of Preparation II as the sole dispersant polymer. The polymer solution from Preparation II, 131.0 g, was mixed with 17.63 g of potassium hydroxide solution (46.4% in deionized water), and 482.8 g of deionized water in a high speed disperser Dispermat® FE (BYK-Gardener, Inc., Silver Spring, Md) for an hour to completely dissolve the polymer. To the polymer solution was added 112.5 g of FW18 carbon black (Degussa Corp., Allendale, NJ), 6.1 g of Proxel® G (Zeneca Inc., Wilmington, DE) as biocide, and 150.0 g of deionized water. The mixture at 15% pigment loading was too viscous to process in the high speed disperser. Deionized water was added to dilute the pigment loading to 12.5%. At this concentration, the mixture became a gel. After stirring for about 15 minutes, the viscosity decreased, and the mixture was stirred at about 5000 rpm in the high speed disperser for an additional hour. The mixture was then dispersed in a microfluidizer (Microfluidics Corp., Watham, MA) by passing it through the interaction chamber 5 times under a liquid pressure of about 7,000 psi. The resulting pigment dispersion had 12.5% pigment concentration with an average particle size of 122 nm as determined by Brookhaven BI-90 particle sizer. The final pH was 8.54.

#### Example 1:

A pigment dispersion was prepared using a blend of polymers prepared as described in Preparations I and II, in the ratio of 10:90 by weight.

The polymer solution from Preparation II, 117.9 g (39% in 2-pyrrolidone), and 51.0 g (10% in deionized water) of the pre-neutralized polymer solution of Preparation I were mixed with 14.29 g of potassium hydroxide solution (46.4% in deionized water), and 328.2 g of deionized water in a high speed disperser Dispermat® FE (BYK-Gardener, Inc., Silver Spring, Md) for an hour to completely dissolve the polymer. To the polymer solution was added, 112.5 g of FW18

carbon black (Degussa Corp., Allendale, NJ) and 6.1 g of Proxel<sup>®</sup> G (Zeneca Inc., Wilmington, DE). The mixture at 22% pigment loading was stirred at about 5000 rpm in the high speed disperser for an hour. The mixture was then dispersed in a microfluidizer (Microfluidics Corp., Watham, MA) by passing it through the interaction chamber 5 times under a liquid pressure of about 7,000 psi. The resulting pigment dispersion had 22% pigment concentration with an average particle size of 107 nm as determined by Brookhaven BI-90 particle sizer. The final pH was 8.15.

With the polymer blend as the dispersant, the dispersion was more easily processed at a higher pigment loading, and the resulting particle size was smaller compared to the control.

#### Example 2:

A pigment dispersion was prepared using a blend of polymers prepared as described in Preparation I and II in the ratio of 5:95 by weight.

The polymer solution from Preparation II, 124.5 g (39% in 2-pyrrolidone), and 25.55 g (10% in deionized water) of the pre-neutralized polymer solution of Preparation I were mixed with 15.08 g of potassium hydroxide solution (46.4% in deionized water) and 284.9 g of deionized water in a high speed disperser Dispermat<sup>®</sup> FE (BYK-Gardener, Inc., Silver Spring, Md) for an hour to completely dissolve the polymer. To the polymer solution was added, 112.5 g of FW18 carbon black (Degussa Corp., Allendale, NJ) and 6.1 g of Proxel<sup>®</sup> G (Zeneca Inc., Wilmington, DE). The mixture was too viscous to process. It was diluted to 18.9% pigment loading with deionized water. The mixture was stirred at about 5000 rpm in the high speed disperser for an hour. It was then processed in a microfluidizer (Microfluidics Corp., Watham, MA) by passing it through the interaction chamber 5 times under a liquid pressure of about 7,000 psi. The resulting pigment dispersion had 18.9% pigment concentration with an average particle size of 106 nm as determined by Brookhaven BI-90 particle sizer. The final pH was 8.17.

With the polymer blend as the dispersant, the dispersion was more easily processed at a higher pigment loading, and the resulting particle size was smaller compared to the control.

#### Control 2:

A pigment dispersion was prepared using the polymer of Preparation III.

133.3 g (15% solution) of the pre-neutralized polymer solution of Preparation III, were stirred with 226.7 g of deionized water and 40 g of FW18 carbon black (Degussa Corp., Allendale, NJ) in a high speed disperser Dispermat<sup>®</sup> FE (BYK-Gardener, Inc., Silver Spring, Md) at about 6000 rpm for an hour. The mixture at 10% pigment loading was viscous. It was forced through the microfluidizer (Microfluidics Corp., Watham, MA) continuously for 90 minutes. No reduction in either particle size or viscosity was accomplished.

#### Example 3:

A pigment dispersion was prepared using a blend of polymers prepared as described in Preparations I and III, in the ratio of 10:90 by weight.

20 g (10% solution) of the pre-neutralized polymer solution of Preparation I, and 120 g (15% solution) of the pre-neutralized polymer solution of Preparation III were mixed with 40 g of FW18 carbon black (Degussa Corp., Allendale, NJ) and 220 g of deionized water in a high speed disperser Dispermat<sup>®</sup> FE (BYK-Gardener, Inc., Silver Spring, Md). The mixture was stirred at about 6000 rpm for an hour. The mixture was then processed in a microfluidizer (Microfluidics Corp., Watham, MA) by passing it through the interaction chamber under a liquid pressure of about 7000 psi. It became viscous first, then with further processing the viscosity gradually decreased. The mixture was passed through the interaction chamber 15 times until an average particle size of 114 nm was obtained. The resulting pigment dispersion has a 10% concentration.

The addition of the random copolymer of Preparation I made this mixture processable.

#### Example 4:

A pigment dispersion was prepared using a blend of polymers prepared as described in Preparations I and III, in the ratio of 15:85 by weight.

30 g (10% solution) of the pre-neutralized polymer solution of Preparation I, and 113.3 g (15% solution) of the pre-neutralized polymer solution of Preparation III were mixed with 40 g of FW18 carbon black (Degussa Corp., Allendale, NJ) and 216.7 g of deionized water in a high speed disperser Dispermat<sup>®</sup> FE (BYK-Gardener, Inc., Silver Spring, Md). The mixture was stirred at about 6000 rpm for an hour and 10 minutes. The mixture was then easily processed with a microfluidizer (Microfluidics Corp., Watham, MA) by passing it through the interaction chamber 8 times under a liquid pressure of about 7000 psi. The resulting pigment dispersion had 10% pigment concentration with an average particle



size of 115 nm as determined by Brookhaven BI-90 particle sizer.

The dispersion process was significantly improved by the presence of the random copolymer.

#### Example 5:

An ink was prepared and tested using the following procedure: The pigment dispersion concentrate of Example 1 was letdown with a vehicle solution to give the following composition.

INGREDIENT	WEIGHT %
Carbon Black, FW18, (Degussa Corp., Allendale, NJ)	2.75
Blend of polymers prepared as described in Preparations I and II (10/90).	1.25
2-Pyrrolidone, Aldrich Chemical Co., Milwaukee, WI	5.0
Liponic® EG-1, Lipo Chemicals Inc., Paterson, NJ.	4.25
N-Methylpyrrolidone, Aldrich Chemical Co., Milwaukee, WI	2.0
Zonyl® FSA (DuPont Co., Wilmington, DE)	0.05
Proxel® G (Zeneca Inc., Wilmington, DE)	0.15
Deionized water	84.6

The ink was filled into a thermal ink jet pen and printed with a Hewlett Packard DeskJet ink jet printer (Hewlett Packard Co., Palo Alto, CA) on Gilbert bond paper (25% cotton, Mead Co., Dayton, OH). It printed smoothly and the print had an extremely high optical density of 1.50 and sharp edges. The print was waterfast immediately after drying.

The ink stability was determined by measuring the particle size change by Brookhaven BI-90 particle sizer (Brookhaven Instrument Corp., Holtsville, NY 11742) after the ink sample had been subjected to 4 temperature cycles, each consisting of 4 hours at -20°C and 4 hours at 70°C. The above ink showed no significant change.

#### Example 6:

Example 5 was repeated with the following exception: the pigment dispersion concentrate of Example 3 was used instead of the pigment dispersion concentrate of Example 1.

The ink was filled into a thermal ink jet pen and printed with a Hewlett Packard DeskJet ink jet printer (Hewlett Packard Co., Palo Alto, CA) on Gilbert bond paper (25% cotton, Mead Co., Dayton, OH). It printed smoothly and the print had an extremely high optical density of 1.55 and sharp edges. The print was waterfast immediately after drying.

The ink appears to be stable. No flocculation was detected after the temperature cycle test.

#### Example 7:

Example 5 was repeated with the following exception: the pigment dispersion concentrate of Example 4 was used instead of the pigment dispersion concentrate of Example 1.

The ink was filled into a thermal ink jet pen and printed with a Hewlett Packard DeskJet ink jet printer (Hewlett Packard Co., Palo Alto, CA) on Gilbert bond paper (25% cotton, Mead Co., Dayton, OH). It printed smoothly and the print had an extremely high optical density of 1.59 and sharp edges. The print was waterfast immediately after drying.

The ink appears to be stable. No flocculation was detected after the temperature cycle test.

#### Claims

1. A process for preparing an aqueous dispersion comprising wet milling an aqueous carrier medium, a particulate solid, and a polymeric dispersant consisting essentially of a mixture of at least one block copolymer and at least one random copolymer wherein:

- (i) the block and random copolymers are prepared from substantially the same monomers; and
- (ii) the random copolymer is present in the amount of 1 to 100 parts by weight per 100 parts by weight of the block copolymer.

2. The process of claim 1 wherein the copolymers have a number average molecular weight less than 20,000.
3. The process of claim 2 wherein the block copolymer is selected from the group consisting of AB, BAB, and ABC polymers.
- 5 4. The process of claim 3 wherein the particulate solid is a colorant and the aqueous carrier medium comprises water and at least one water soluble organic component.
- 10 5. The process of claim 4 wherein the wet milling is accomplished in a media mill.
6. The process of claim 4 wherein the wet milling is accomplished by passing the aqueous carrier medium, particulate solid and the polymeric dispersant through a plurality of nozzles within a liquid jet interaction chamber under a liquid pressure of at least 1000 psi.
- 15 7. An aqueous dispersion containing an aqueous carrier medium, a particulate solid, and a polymeric dispersant consisting of a mixture of at least one block copolymer and at least one random copolymer wherein:
  - (i) the block and random copolymers are prepared from substantially the same monomers; and
  - (ii) the random copolymer is present in the amount of 1 to 100 parts by weight per 100 parts by weight of the block copolymer.
- 20 8. The dispersion of claim 7 wherein the copolymers have a number average molecular weight less than 20,000.
9. The dispersion of claim 8 wherein the block copolymer is selected from the group consisting of AB, BAB, and ABC polymers.
- 25 10. The dispersion of claim 9 wherein the particulate solid is a colorant and the aqueous carrier medium comprises water and at least one water soluble organic component.
- 30 11. The dispersion of claim 10 wherein the copolymers have a number average molecular weight less than 20,000.
12. The dispersion of claim 11 particularly adapted for use as an ink for ink-jet printers.
- 35 13. An ink particularly adapted for use with an ink-jet printer, said ink consisting essentially of:
  - (a) approximately 25 to 99.8% of an aqueous carrier medium comprising water and at least one water soluble organic component;
  - (b) approximately 10 to 60% of a particulate colorant having a particle size less than 15 microns; and
  - (c) approximately 0.1 to 30% of a polymeric dispersant consisting of a mixture of at least one AB, BAB, or ABC block copolymer and at least one random copolymer wherein:
    - (i) the block and random copolymers are prepared from substantially the same monomers; and
    - (ii) the random copolymer is present in the amount of 1 to 100 parts by weight per 100 parts by weight of the block copolymer;
- 40 45 wherein said percentages of components (a), (b) and (c) are of the total ink composition.
14. The ink of claim 13 wherein the copolymers have a number average molecular weight less than 20,000.
- 50 15. The ink of claim 13 wherein component (c) is present in the amount of 0.1 to 15% by weight, has a number average molecular weight below 10,000, and the ratio of block copolymer to random copolymer in the range of 100 to 1 parts block copolymer per 1 part random copolymer, by weight.
- 55 16. The ink of claim 15 wherein component (a) is present in the amount of 70 to 96% and contains a water-soluble organic solvent.
17. The ink of claim 15 wherein said block copolymer and random copolymer are anionic.

18. The ink of claim 15 wherein said block copolymer and random copolymer are cationic.

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**(54) Two component dispersant for wet milling process**

(57) A process for preparing an aqueous dispersion by wet milling an aqueous carrier medium, a particulate solid, and a polymeric dispersant; wherein the polymeric dispersant is a combination of at least 50% by weight of a block copolymer; and a random copolymer; and wherein the block and random copolymers are prepared from substantially the same monomers. This invention provides an easy dispersion process for particulate solids, in particular colorants such as pigments or disperse dyes, at higher loadings, and a reduction of dispersion time which improves the productivity. Resulting dispersions have particular utility as inks for ink-jet printers.

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# EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
E	DATABASE WPI Week 9748 Derwent Publications Ltd., London, GB; AN 520950 XP002075711 "disperse inorganic powder contain water soluble co condensate water soluble polymer random copolymer chain" * abstract * & JP 09 248 438 A (KAO) ---	1	C09D17/00 C09D11/00
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A	DATABASE WPI Week 9443 Derwent Publications Ltd., London, GB; AN 347262 XP002075712 "propylene type resin composition colour propylene" * abstract * & JP 06 271 741 A (TOKUYAMA) ---	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C09D C08L
A	DE 43 28 215 A (E.I. DU PONT DE NEMOURS) 3 March 1994 * page 2, line 56 - page 5, line 22; claims 1,2; examples * ---	1	
A	US 5 519 085 A (MA ET AL) 21 May 1996 * column 2, line 21 - column 7, line 3; claims 1-25 * ---	1	
A.D	US 5 085 698 A (MA ET AL) 4 February 1992 * column 2, line 14 - column 7, line 7; claims * ---	1	
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>27 August 1998</b>	Examiner <b>Bourgonje, A</b>
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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# EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D, A	US 5 219 945 A (DICKER ET AL) 15 June 1993 * column 1, line 60 - column 4, line 4; claims *  -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>27 August 1998</b>	Examiner <b>Bourgonje, A</b>
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			

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